VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ

Fakulta chemická

# DIPLOMOVÁ PRÁCE

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# VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ
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## FAKULTA CHEMICKÁ
FACULTY OF CHEMISTRY

## ÚSTAV FYZIKÁLNÍ A SPOTŘEBNÍ CHEMIE
INSTITUTE OF PHYSICAL AND APPLIED CHEMISTRY


# VLIV FOTOCHROMNÍHO ADITIVA NA OPTICKÉ A ELEKTRICKÉ VLASTNOSTI POLYMERNÍCH MATRIC

INFLUENCE OF PHOTOCHROMIC ADDITIVES ON THE OPTICAL AND ELECTRICAL PROPERTIES OF POLYMER MATRICES

**DIPLOMOVÁ PRÁCE**
MASTER'S THESIS


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# Zadání diplomové práce

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## Název diplomové práce:

Vliv fotochromního aditiva na optické a elektrické vlastnosti polymerních matric

## Zadání diplomové práce:

Práce je zaměřena na přípravu a charakterizaci tenkých vrstev polymerních materiálů s polovodičovými vlastnostmi. Studován bude vliv fotochromního spiropyranu na jejich základní optické a elektrické vlastnosti. Pozornost bude věnována rovněž možnostem ovlivnění procesů fotogenerace a transportu náboje v těchto matricích.

Postup řešení:

1. Proveďte rešerši na zadané téma, zaměřte se na články a moduly vhodné pro průmyslové aplikace a vztah mezi jejich strukturou a výslednými parametry.
2. Připravte tenké vrstvy vybraných materiálů.
3. Charakterizujte základní optické, elektrické a další vlastnosti připravených vrstev s ohledem na vliv fotochromního spiropyranu na tyto vlastnosti.
4. Získané výsledky vyhodnoťte.

## Termín odevzdání diplomové práce: 5.5.2017

Diplomová práce se odevzdává v děkanem stanoveném počtu exemplářů na sekretariát ústavu. Toto zadání je součástí diplomové práce.

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| Bc. Šárka Tumová<br>student(ka) | prof. Ing. Martin Weiter, Ph.D.<br>vedoucí práce | prof. Ing. Miloslav Pekař, CSc.<br>vedoucí ústavu |

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děkan

V Brně dne 31.1.2017

## ABSTRAKT

Tato práce se zabývá fotochromní molekulou spiropyranu, která osvícením UV lampou mění svou strukturu a také fyzikální a chemické vlastnosti. Tyto změny jsou vratné, molekula se při mírném zahřívání vrací zpět do své původní formy. Pro studium byla zvolena fotochromní molekula SP1, jejíž systematický název je: 1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2'-(2*H*)-indole]. Tato molekula byla včleněna do polymerů PVK, Tg PPV, PCBTDPP a PCBTDPP a pomocí metody UV-VIS spektroskopie byla sledována fotochromní aktivita v těchto matricích. Byl pozorován vliv prostředí molekuly na její schopnost fotochromní konverze stejně jako na teplem vyvolanou vratnou reakci. Dále bylo zkoumáno, zda tato struktura ovlivňuje elektrické vlastnosti jednotlivých polymerů. Studován byl vliv fotochromní konverze jak na pohyblivost nosičů nábojů, tak na jejich fotogeneraci v rámci polymeru. Pro posouzení efektu konverze spiropyranu na elektrické vlastnosti polymerní matrice bylo využíváno metody volt-ampérových charakteristik.

## ABSTRACT

This thesis is focused on the photochromic molecule of spiropyran, which changes its structure as well as physical and chemical properties after UV irradiation. These changes are reversible, the molecule thermally restore its initial structure. For the study, the molecule SP1 with the systematic name 1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2'-(2*H*)-indole] was used. This molecule was incorporated within polymers PVK, Tg PPV, PCBTDPP and PCDTBT and the method of UV-VIS spectroscopy was used to observe the photochromic activity within these matrices. The influence of matrices to the ability to undergo UV induced photochromic conversion as well as to the reverse conversion to the initial structure induced by heat was monitored. Furthermore, the influence of spiropyran to the electrical properties of individual matrices was studied. The effect of photochromic conversion to both, the mobility of charge carriers and to the photogeneration was observed. For this purpose, the method of current-voltage measurement was used.

## KLÍČOVÁ SLOVA

Fotochromismus, spiropyran, fotogenerace, UV-VIS spektroskopie, volt-ampérové charakteristiky

## KEYWORDS

Photochromism, spiropyran, photogeneration, UV-VIS spectroscopy, current-voltage characteristics

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## PROHLÁŠENÍ

Prohlašuji, že jsem diplomovou práci vypracovala samostatně a že všechny použité literární zdroje jsem správně a úplně citovala. Diplomová práce je z hlediska obsahu majetkem Fakulty chemické VUT v Brně a může být využita ke komerčním účelům jen se souhlasem vedoucího diplomové práce a děkana FCH VUT.

……

podpis studenta


## Poděkování

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# 1 Introduction

The molecule of spiropyran is interesting due to its ability to undergo photochromic conversion, i.e. reversible change of its structure and therefore of its chemical and physical properties induced by electromagnetic radiation (in the case of spiropyran by UV light). The phenomenon of photochromism has become an interesting issue of researches, finding its utilization in the variety of aesthetic and functional applications and in production of a diverse array of niche products.

Photochromism may originate from a range of different molecular transition and can occur in both organic and inorganic compounds, in solids as well as in solutions. However, photochromic compounds in general are very sensitive to their environment. The mode of incorporation, intermolecular interaction, variation in the polarity, free volume as well as rigidity of the matrix, it is all more or less imposing steric restrains by limiting the mobility of the photochromic molecule within the polymeric matrix and therefore it all affects the photochromic response. On the other hand, the photochromic molecule may transfer the reversible changes of its physical or chemical properties to its environment and so to cause its modification.

The main goal of this thesis was to incorporate the photochromic spiropyran SP1 into various polymeric matrices, namely into polymers PVK, Tg PPV, PCBTDPP and PCDTBT, and to observe if the presence of this structure leads to the change of its properties, attention was paid especially to the optical and electrical properties. Therefore, the thin layers of pure polymeric materials as well as layers of spiropyran-doped materials were prepared and their optical and electrical properties before and after UV-induced photochromic conversion were studied. The optical characterization was focused to the ability of spiropyran to undergo UV induced photochromic conversion within particular matrix as well as to the reverse conversion of merocyanine form to its initial structure induced by heat. The method of UV-VIS spectroscopy was used to identify the open and closed form of spiropyran. The electrical characterization was focused on the effect of photochromic conversion and so of photoswitchable charge carrier traps to the mobility of charge carriers as well as to the photogeneration. For this purpose, the method of current-voltage measurement was used.

# 2 Theoretical Part

## 2.1 Photochromism

The phenomenon of photochromism is defined as a reversible transformation of chemical species between two isomeric forms, induced at least in one direction by electromagnetic radiation [1],[2]. Generally, the activating radiation is in the UV region (300 to 400 nm) but could be in the visible one as well (400 to 700 nm) [3].The absorption of light by photochromic compound causes a change in its conformation or molecular structure, which results in a change of absorption spectra. The characteristic that identifies photochromism from other photophysical processes is thermal or light induced reversibility, so the original isomeric form can be restored by exposure to light or heat. The photochromic interconversion between isomeric forms is often referred to as switching. A typical photochromic system can be represented by the Figure 1 [1],[2]. Photochromism can occur in both organic and inorganic compounds, in solids as well as in solutions. Organic molecular families that are known to exhibit photochromism include spiropyrans, spirooxazines, fulgides, diarylethenes, viologens and azocompounds. The photochromism of inorganic compounds is based on electron transfer in the crystalline state [4]. This phenomenon can be observed on systems such as metal oxides, alkaline earth metals, mercury compounds and transition metal compounds [1].

$$\mathrm{A}(\lambda_1) \underset{h\upsilon_2 / \Delta}{\overset{h\upsilon_1}{\leftrightarrow}} \mathrm{B}(\lambda_2) \tag{1}$$

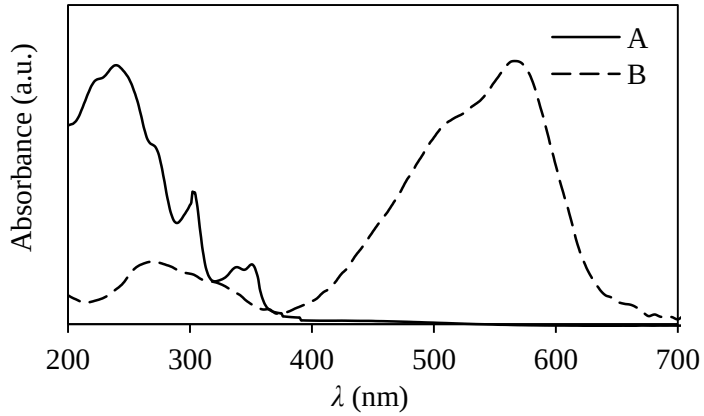



*Figure 1: Photochromic reversible transformation of a chemical structure between two forms, A and B, having different absorption spectra [2].*

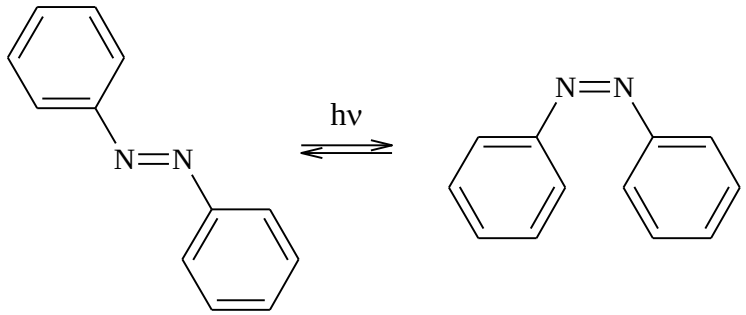
As mentioned above, the main criterion for photochromism is reversibility [3]. We distinguish two types of photochromism according to the mechanism of the back reaction [4]. First is T-type photochromism when the back reaction is driven thermally as is the case of, for example, spiropyrans, spirooxazines and chromenes. If the photochromic structure reverts back to its original state after irradiation by another range of wavelengths, i.e. the change occurs by photochemical mechanism, then it is referred to as P-type photochromism. This includes systems as fulgines or arylethenes[3],[5].

There are also some special types of photochromism, for example gated and dual-mode photochromism. In the case of gated photochromism, one or both isomeric forms are reversibly transformed into a form that is nonphotochromic. Dual-mode photochromism takes place within complex systems triggered alternatively by two different external stimuli, for example light and electrical current, then, photochromism and electrochromism are mutually regulated [6].

### 2.1.1 Mechanisms of the Photochromic Reactions

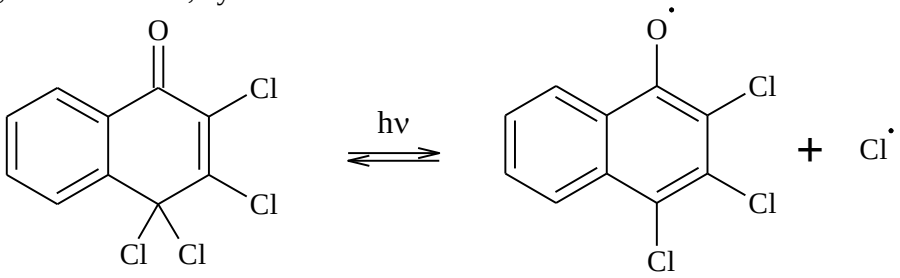
The photochromic transformation and the observed spectral changes or changes in physical or chemical behaviour are related to the modifications of the geometry of the system and its electronic distribution [3]. It can originate from a range of different molecular transitions [1], [2], [6] – [8]:

- Cis-trans isomerisation – after the absorption of the certain wavelengths, the structure changes its spatial arrangement from stable trans isomer to less stable cis isomer. This chemical process occurs in stilbenes, azocompounds, azines, etc., as well as in some photochromic biological receptors that are part of living systems.



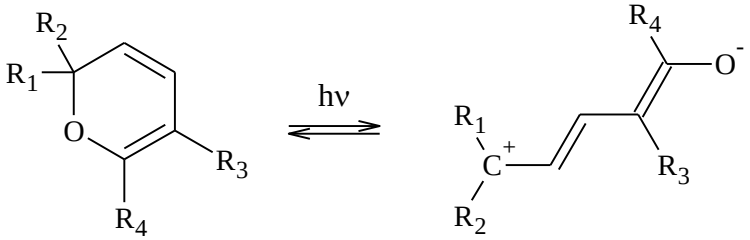

(2)

- Homolytic and heterolytic bond cleavage – irradiation of the structure causes splitting of its chemical bond. In the case of homolytic cleavage, each fragment gets one of the shared electrons, so products are predominantly radicals. This process is found in triarylimidazole dimmers, nitrosodimeres, hydrazines etc.



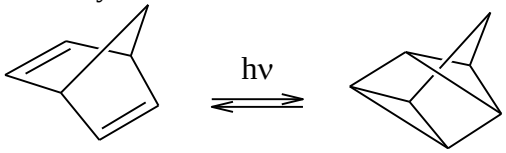

(3)

During heterolytic cleavage one atom gets both of the shared atoms. This occurs in spiropyrans, spirooxazines, fulgines or triarylmethanes and related systems.




(4)

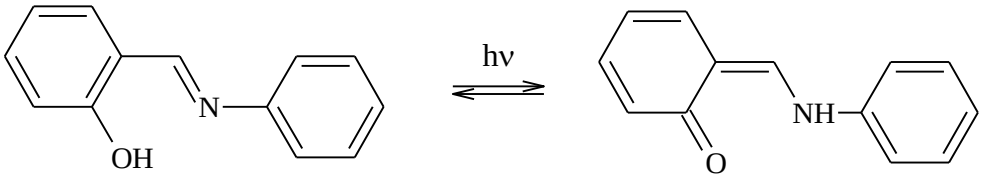
- Pericyclic reactions – spiropyrans, spirooxazines, chromenes etc. can undergo electrocyclization, when π-bond of the conjugated system splits and σ-bond is formed between two atoms of this system, which causes the cyclization.




(5)

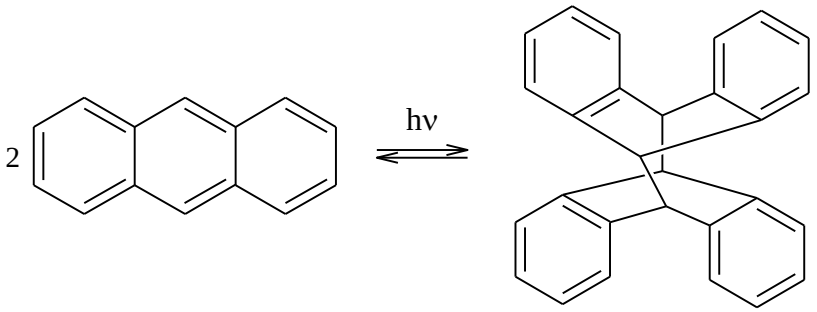
In some other structures, cycloaddition can be found. During this reaction, two π-bonds split and two σ-bonds are formed.

- Intramolecular hydrogen, group and electron transfer – intramolecular hydrogen transfer is found in anils, benzylpyridines, salicylates, triazoles, oxazoles, metal dithizonates and perimidinespirohexadienones; intramolecular group transfer operates in polycyclic quinines and electron transfer (oxido-reduction) is photoinduced in viologens and related systems.
- Tautomeric photochromism – this chemical process can be defined as a balance between isomers that are produced by conformational, configuration and constitutional conversions. The coloured form is stabilized by interaction of the photochromic material with its environment.




(6)

- Triplet-triplet photochromism – this process is characteristic for condensed aromatic molecules. During the interaction between radiation and matter, electrons are excited to the triplet state that is stable enough to absorb certain wavelengths.
- Photodimerization – polycyclic aromatic hydrocarbons and aromatic heterocycles can undergo photodimerization, when excimers are formed after irradiation.




(7)

### 2.1.2 Photophysics of Photochromic Compounds

If a molecule is in its ground state, electrons are predominantly in their lowest electronic state. After absorption of electromagnetic radiation, they are promoted to higher energy levels, so the excited states are formed. These states depend on the energy of the interacting photon [1], [2]. Most often, the photochromic processes are one-photon mechanisms. The photoproduct is then formed form the singlet excited states, triplet excited states or from both of them. The transition to the excited state can also occur by absorption of two photons. In this case, two processes of absorption can be distinguished, see Figure 2 [6]:

- Simultaneous absorption of two photons via virtual level
- Stepwise two-photon absorption where the absorption of the second photon takes place from a real level

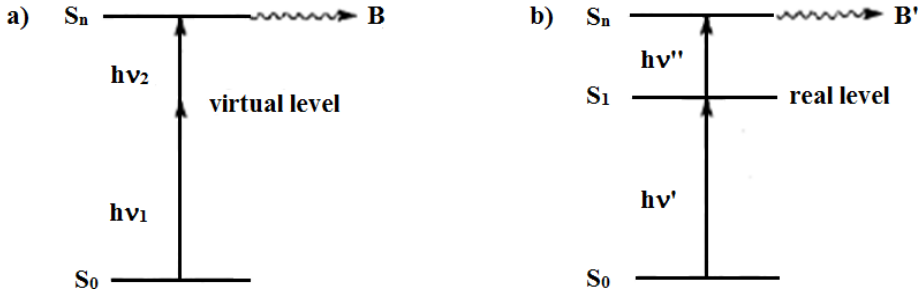



*Figure 2: Simultaneous (a) and stepwise (b) two-photon absorption leading to product B or B'.*

The lifetime of the excited state is brief; the molecule can release excess energy by several relaxation processes. The most common relaxation involves radiative and non-radiative pathways. Other possibility is thermal deactivation by vibrational relaxation or energy transfer to the environment of the molecule, see Figure 3 [1], [2], [4].

The radiative pathways are characterised by transition of the molecule to the lower energetic state that is accompanied by the emission of the quantum of energy in the form of photon. There are more types of this relaxation pathway [1], [2], [4], [6]:

- Fluorescence – the radiative transition to the lower energy level with the same multiplicity. It is indicated on a Jablonski diagram as a straight line going down on the energy axis between electronic states. There are some special types of this transition, for example delayed fluorescence.
- Phosphorescence – another radiative pathway for molecules to deal with energy received from photons. It is a transition to the lower energy level with different multiplicity.

In the case of photochromic system, there is another possibility of radiative deactivation, namely it is photoreaction, when molecule uses the absorbed energy to change its conformation [1], [2], [6]

During non-radiative deactivation pathways, the energy of the system remains unchanged. It is a crossing between isoenergetic vibrational-rotational levels of different electronic states. Internal conversion (transition between states with the same energy and multiplicity) and intersystem crossing (transition between states with the same energy but different multiplicity) are the most common non-radiative relaxation processes [4].

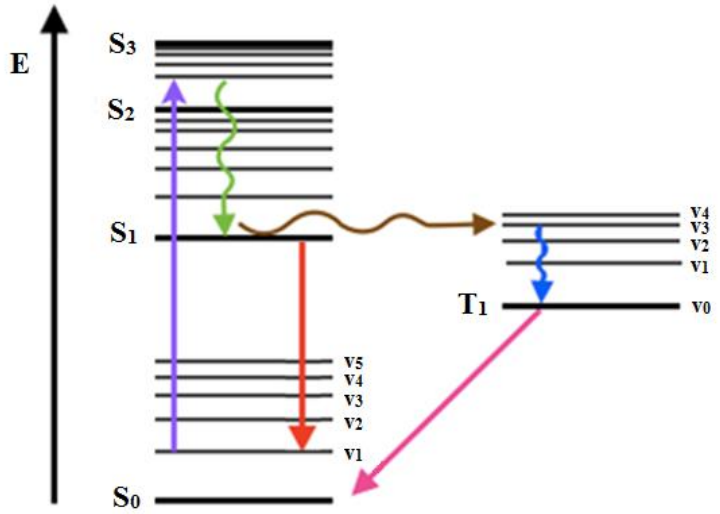



*Figure 3: Jablonski diagram [9]shows several different pathways how an electron may accept and then dissipate the energy from a photon of a particular wavelength, not including photochromism; purple line indicates absorption of energy, green one refers to internal conversion, brown shows intersystem crossing, blue indicates vibrational excitation, pink refers to phosphorescence and red line depicts fluorescence.*

The path of deactivation the molecule takes depends on kinetics of the system and on the environment of the molecule. If the photochromic reaction is fast and efficient enough to overcome all other photophysical processes it must happen within the lifetime of the excited singlet or triplet state. In this sense any radiative transitions can be considered as competitive deactivation pathways [1], [2], [6].

### 2.1.3 Effect of Molecule Environment

Photochromic compounds in general are very sensitive to their environment. The behaviour of the photochromic molecules is then interconnected with polymer matrix on many levels which is offering the potential for modifying the kinetics to suit different applications. The mode of incorporation, intermolecular interaction, variation in the polarity, free volume and rigidity of the matrix, as well as ambient temperature, it all affects the response of photochromic structure. All of these effects are more or less imposing steric restrains by limiting the mobility of the photochromic molecule within the polymer matrix so the ability to isomerise is reduced [1], [2]. It is also the reason, why the photochromic transition is slower in a polymer matrix, as compared to solution.

#### *2.1.3.1 Incorporation of Photochromic Compound*

In a general sense, photochromic compounds may be incorporated into a polymer in two ways, either by covalent bonding to the bulk matrix or by doping/dispersing within it. Moreover, two different approaches how to covalently bond the photochromic to the polymer can be distinguished. The first one is incorporation as a side group; the second is to attach polymerizable groups to the photochromic and let it copolymerize with other monomers. The use of controlled radical polymerization techniques offers possibilities to synthesize photochromic polymers with defined characteristics. This method has become an efficient tool, that enables to design polymers in a more predictable and controlled way and with a range of architectures [1], [2].

Specific studies focused on investigating the difference that the two ways of incorporation of photochromic into the matrix would have on photochromic performance were carried out. One of them is research conducted by Lyubimov *et al.* [10] that shows different results depending on the way of photochromism incorporation. There were some differences between absorption spectra of copolymer and mixture films. Significant differences were observed at dark decolouration process of their doped and bonded model, when the kinetics of thermal fading of copolymer film was multi-exponential, while mixture film displayed first-order kinetics, see Figure 4.

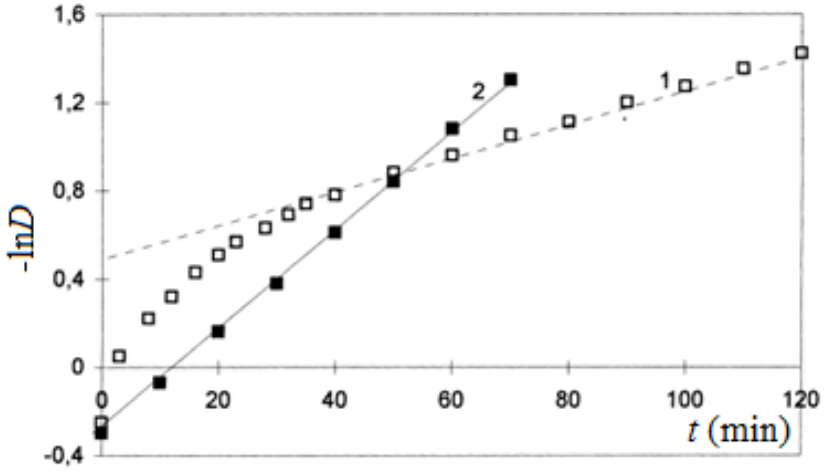



*Figure 4: Kinetics curves of the dark decolouration for the bonded (1) and doped (2) model, where D is the optical density at absorption maximum of the photoproduct [10].*

Photochromic compounds have been doped into a full range of organic polymers, with some interesting works also in inorganic systems and in combination inorganic/organic matrixes [11] – [18].

### *2.1.3.2 Effect of Polarity*

The two isomeric forms of photochromic compound, the original structure and photoproduct, differ in polarity, thus polarity of a matrix is an important factor that is having a big impact on photochromic kinetics, especially on decolouration rate within polymer matrices. One of the isomeric forms may be preferentially stabilized, so the equilibrium between them is influenced by the polarity of the matrix. When the matrix contains polar groups, the polar photoproduct may become preferably stabilized, which is leading to larger activation energy of back reaction and therefore a slower reversion back to the original structure in comparison with non-polar matrix. This is a case of spiropyran. Its open form (merocyanine) is more polar, therefore, the rate of decolouration decreases in polar matrix. The more polar matrix, the more stabilized merocyanine form is. The more stabilized merocyanine form, the slower the decolouration is. Occasionally, the stability of merocyanine form can be enhanced by other factors (salvation, hydrogen bonding…), then, coloured form occurs before irradiation. This phenomenon is termed reverse photochromism [1], [2]

Some studies focused on investigating how the polarity affects photochromic kinetics were carried out. One of these studies was focused on photochromism in the two-phase solution [19]. The solution consisted of polar droplets and non-polar oil. After adding the spiropyran, multicolour solution exhibiting three states with different colours depending on the irradiation, was prepared, see Figure 5.

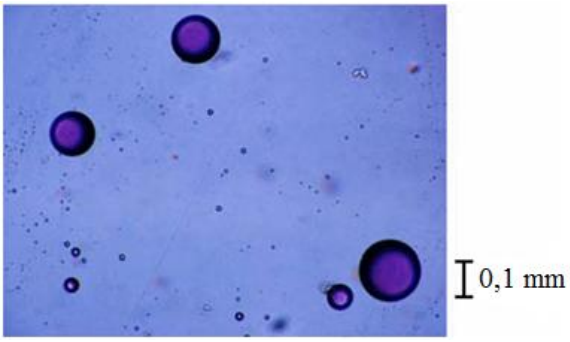



*Figure 5: Solution consisted of polar droplets and non-polar oil after irradiation with UV light [19].*

This dependence of spiropyran properties on polarity of environment was used to create capillaries that are able to photoidentify solvents with different polarity [20]. The surface of fused silica microcapillaries was functionalized with spiropyran-polymer brushes. Solvents with different polarity can be easily detected while passing through it by simply irradiating with UV light; spiropyran is converted into merocyanine form and microcapillary gains a distinct colour and spectral response depending on the polarity of the solvent, see Figure 6.

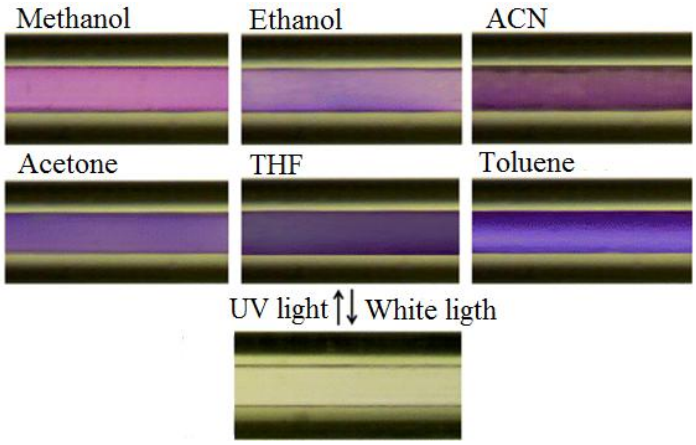



*Figure 6: Microcapillary containing spiropyran when irradiated by UV light while different solvents are passed through and after irradiation with white light [20].*

### *2.1.3.3 Effect of Rigidity and Free Volume*

Rigidity and free volume of the system are other effects that impose restriction to the photochromic kinetics. It was shown that closely spaced photochromic groups in a copolymerized system may hinder the reaction of photochromic by limiting the free volume that is needed for the photochromic transition and the segmental movement of polymer chains [6]. The behaviour of spiro-compounds has been investigated in the entire range of matrices, from flexible to more rigid glassy systems [18], [21]. Most of these researches proved the expectation that the decolouration rate is the slower the more rigid the system is. There are also some exceptions that show, that in very rigid glass matrices the decolouration rate is unusually high [22]. It was justified by the presence of coloured species in strained conformation which failed to push rigid environment around itself. In the research conducted by Such [23] the 2 component system (one component rigid, other flexible) was used to show control over the switching rate through the rigidity of matrix. The tuneable decolouration rate (from 178 to 5 s) was achieved by varied ratio of components, see Figure 7. Photochromic compounds are commercially used, among others, for the photochromic ophthalmic industry. In this case it is necessarily to make products with performance characteristics acceptable to the consumer. Unfortunately, the effect of rigidity causes slow rate of decolourization after irradiation, thus there are also some researches focused on optimizing the photochromic switching in rigid matrices [24], [25].

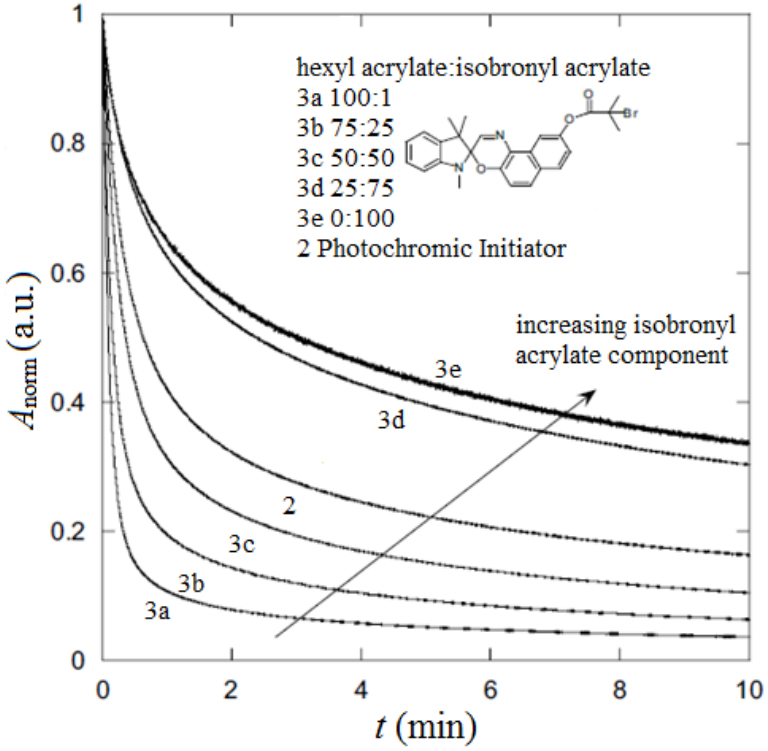



*Figure 7: Decolouration rates of the series of copolymer-spirooxazine conjugates; increase in isobornyl acrylate causes an increase in rigidity [23].*

### 2.1.4 Spiropyran

The molecule of spiropyran consists of two moieties; there is always chromene portion and the second one is usually (but not necessarily) heterocyclic. These two parts are orthogonally linked through a spiro-carbon atom in $sp^3$ hybridisation, which is common to both rings and electronically insulates half of the molecule from the other. Therefore, the π-electrons in both halves of the molecule do not interact with each other so, the absorption spectrum is the sum of both of their spectra. After irradiation by UV light, the carbon-oxygen bond is broken (heterolytic cleavage), the hybridisation of insulating carbon atom is changed to $sp^2$ and an extensive conjugated system

is created. This is accompanied by a rotation of the two parts of the spiropyran molecule resulting in the formation of a planar structure with intensive colour. This structure is referred to as merocyanine or open form [1] – [3]. As was mentioned above, it is possible to restore initial closed form thermally or photochemically. Actually, there is always a dynamic equilibrium between the two forms of spiropyran, open and close. Irradiation with UV light just shift the balance so that the concentration of the merocyanine form increases, which may be observed as intensifying of colour. On the other hand, after removal of the light source, the decay of the open form to the close one is promoted, which leads to the reduction of the intensity of colour – fading [5]. Merocyanine can also be irreversibly bleached by reaction with some added reagent [3].

Merocyanine structure may be represented by a mixture of resonant forms, either zwitterionic, delocalized or keto form, see Figure 8. The immediate predominant merocyanine form is depending on substituent and polarity of the surrounding environment. As was mentioned above, merocyanine interacts strongly with the polar matrix, which leads to the stabilization of this form. The zwitterionic form is the most polar one, therefore its stabilization in polar matrix is the most effective [1], [2].

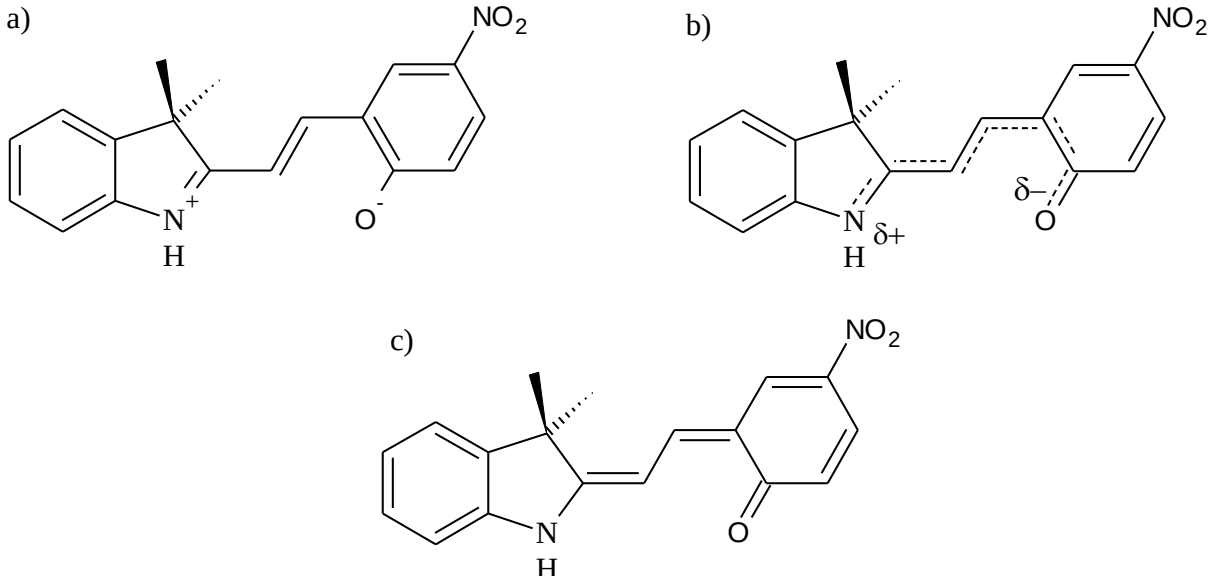



*Figure 8: Possible merocyanine structures; zwitterionic (a), delocalised (b) and keto form [2].*

The merocyanine itself is an equilibrium mixture of geometrical conformations formed by double bond rotation, depending on the geometric arrangement of the two halves of the molecules with respect to the conjugated bridge in between. There are 8 possible isomers of the open structure that can be formed after irradiation, however only 4 of them represent a local energy minimum and are therefore consider to be stable isomers. It is TTC (trans trans cis), CTC (cis trans cis), TTT (trans trans trans) and CTT (cis trans trans) isomer, as shown in Figure 9 [1] – [3]. Some studies focused on the stability of merocyanine isomers were carried out. Methods such as thermodynamic calculations [26] and Nuclear Overhauser Effect (NOE) measurements [27] were used and based on them it was determined that the most stable isomer is the TTC.

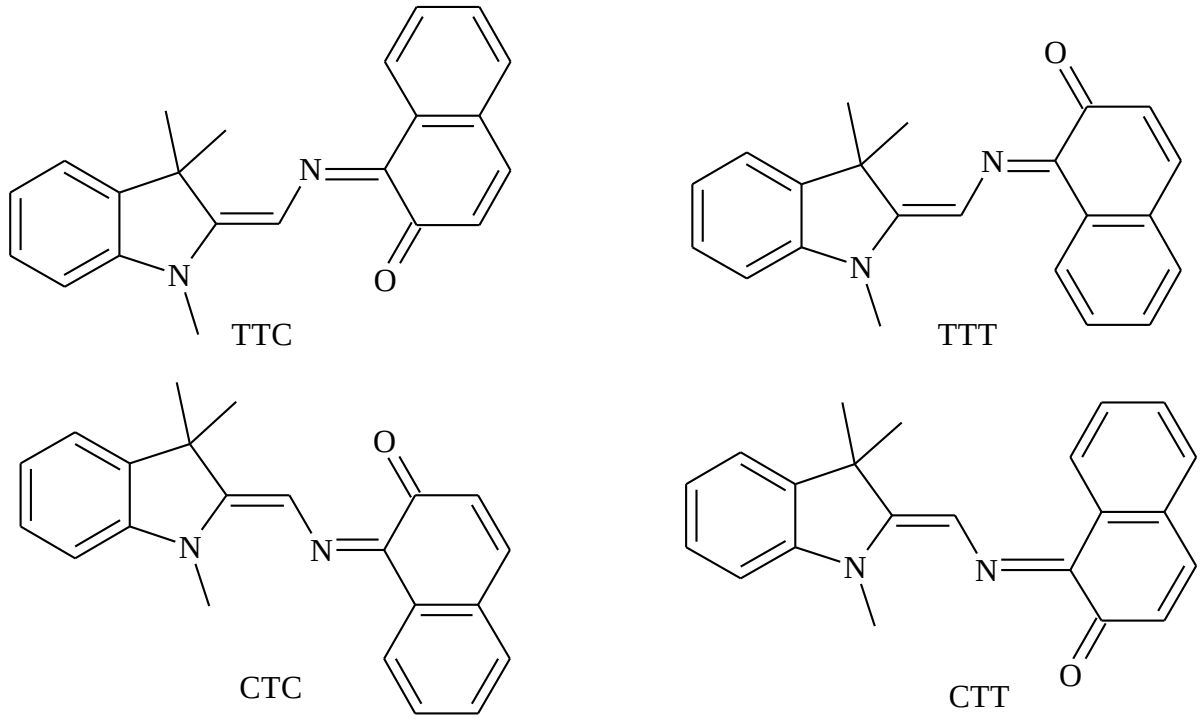



*Figure 9: Stable merocyanine isomers [1].First letter refers to the first double bond in the centre of the molecule starting on the indole side, the second to the next single bond that can rotate to produce different structure and the third to the second double bond.*

The photochromic conversion is associated with the charge redistribution leading to the increase of the dipole moment of the open form. Due to the different conformation, the dipole moment of all of the possible merocyanine isomers reaches another value. Such dipole moment acts as a trap for charge carriers within the polymer chain, the higher the dipole moment, the greater the depth of the trap. The charge carriers may be captured within the trap from where they may be released once they have enough energy. Therefore, the deep traps can considerably affect the mobility of charge carriers, where the mobility expresses their ability to move through a conducting material. The photochromic molecule may transfer the reversible changes of its physical or chemical properties to the environment and supramolecular structure and so to cause its modification. While the photochromic molecule is incorporated within the polymeric matrix, the dipole moment contributes to the modification of the ionization energy and therefore of the polarization energy of the polymer segments near the dipole. This may lead to the local decrease of the ionisation energy representing trap for hole, see Figure 10. The depth of such hole $E_P$ is the difference between ionisation energies of the polymeric matrix with localised charge created by the photochromic conversion $I_{c2}$ and of the perfect polymeric matrix $I_{c1}$ [28], [29]:

$$E_P = I_{c2} - I_{c1} \tag{8}$$

The ionisation energy of the perfect polymeric matrix $I_{c1}$ is related to the one of isolated spiropyran molecule $I_g$ together with the polarization energy $P_1$ of the interaction of the charge carrier within the crystal lattice and surrounding polarisable grid:

$$I_{c1} = I_g - P_1 \tag{9}$$

The charge carrier will be localised at the place of local higher absolute value of polarization energy $P_2$ then the one of perfect polymeric matrix [28], [29].

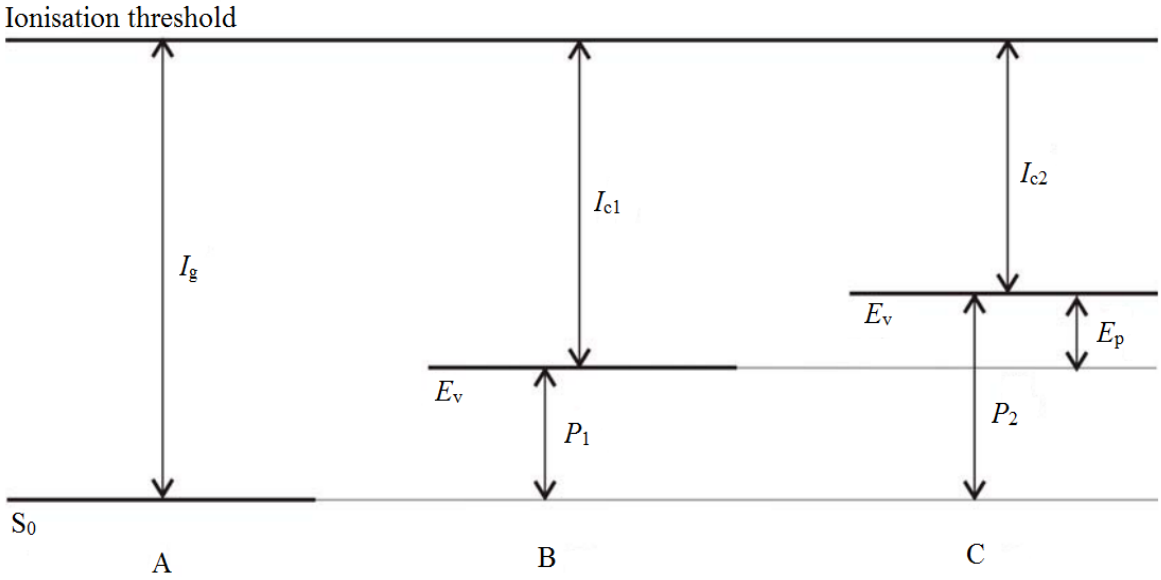



*Figure 10: Energetic diagram shows the ionisation energies of isolated spiropyran $I_g$ (A), perfect polymeric matrix $I_{c1}$ (B) and polymeric matrix with localised charge created by photochromic conversion $I_{c2}$ (C). This conversion leads to the increase dipole moment, which causes increased polarisation energy from $P_1$ to $P_2$. The difference between these energies corresponds to the energy of created trap hole $E_p$ [28].*

In the case of systems with a disordered distribution of photochromic, such as its distribution within polymer matrix volume, the decrease of the mobility of charge carriers occurs due to the expanding of distribution of transport levels [28], [29].

## 2.2 Application of Photochromic Compounds

It is not surprising, that thanks to the ability to darken in the light and recover its transparency away from bright light, photochromic molecules find the worldwide commercial application in ophthalmic lenses. This application made the photochromism a familiar term. Much effort was targeted to utilize the photochromism for variety of aesthetic and functional applications and it found a use in production of a diverse array of niche products. Photochromic systems are still the subject of much industrially funded research into nascent high-tech applications [1], [2], [5]. Great attention has been devoted to the researches concerning to the surface coatings [30], novelty items and various light transmissible materials, mostly to provide UV protection [31] or noticeable visual effect [2]. An interest of the researches was also attracted by applications such as stimuli-responsive materials [32], high-density optical data storage [33], [34], optical memories [35], [36], optical displays and so on. Photochromic compounds are also involved to the preparation of photo-responsive nanostructure polymers [37]. In such supramolecular or polymeric assemblies the photoinduced alterations may cause changes in micro environment [6].

As was mentioned above, photochromic compounds are very sensitive to their environment, thus it has to be incorporated into media in such way that photochromic effects with desire colour, kinetics and resilience are created [5]. On the other hand, some applications exploited photomechanical effects that are induced by the conformational changes of polymeric environment. These changes lead to the crosslinking, aggregation or crystallization of the macromolecules and thus to the different behaviour of photochromic compound [6]. Some developments also combine photochromism with other phenomena. An example is combining the photochromic electron transfer reaction of viologens with electrochemistry [3].

Two types of application may be distinguished [3], [6]:

- Applications in which the colour change caused by the molecular and electronic structure of the two isomeric forms is crucial. These applications are based on the diverse absorption and emission spectra of the close and open form. It is for example photochromic ophthalmic lenses, camera filters, optical information storage or security printing inks.
- Applications that are related to changes of the physical or chemical properties that occur after irradiation of photochromic structure, such as conductivity, refractive index, electrical moment, solubility, surface wettability or viscosity. These changes are used for example in optoelectronic systems, reversible holographic systems or photochemical switchable enzymatic systems.

### 2.2.1 Ophthalmic Lenses

As has already been indicated, photochromic plastic ophthalmic sunglasses are the largest volume and value application for photochromic compounds. They are used to protect the human eyes against the bright light, but similar tool is also used to protect optical sensors from the damaging effects of the intense flashes of light [6]. For this application, the speed and colour of photochromic transition is important [1]. An ideal compound becomes suddenly opaque during exposure to the light and immediately transparent again at the end of the light exposure [6].

In a general sense, photochromic compounds (dye) may be incorporated into lenses in two ways [5]:

- Formation of photochromic layer – the front or the back side of the lens may be coated with photochromic dye by spin- or dip-coating. Another technique used for this purpose is to laminate a film that contains photochromic dye between two sides of lens.
- Incorporation into the polymer matrix – dye may be injection-moulded in a thermoplastic or dissolved in a monomers or resin system which is then thermally or UV-cured. Dye can also be allowed to diffuse into a polymer matrix.

In the case of incorporation into matrix, the polymer is of crucial importance as it has to allow dye molecules to function within the matrix. Conventional plastic lens materials, like polycarbonate, are too rigid [5]. Photochromic dyes, on the other hand, generally underwent rapid photodegradation which is a serious deficiency [3]. Therefore, researches leading to innovations and development of systems with great compromise of matrix and dye properties are carried out [5]. One of the innovations is photochromic lenses made especially for drivers. These lenses are activated by both UV and visible light, depending upon whether or not the sunlight was filtrated through a car windscreen, and change to different hues. This two-step activation is achieved by use of a combination of photochromic structures with diverse absorption spectra. After irradiation under the windscreen the lens becomes only copper-coloured, thus it helps to remove excess light while not influence traffic signal recognition [5], [38].

### 2.2.2 Surface Coating

Photochromic inks and varnishes found their application in a wide range of aesthetic products, but their properties have been used for more functional application as well. For example, there are some studies focused on the photochromic inks for digital inkjet printing [39] or for printing system based on the “write–erase–write” concept [40]. This concept is eco-friendly as it used photochromic inks to produce colour images that will erase after irradiation with visible light without affecting the quality of the paper, see Figure 11. The print–erase cycles can be carries multiple times without deterioration of the quality of the next images, so it allows rewriting paper multiple times.

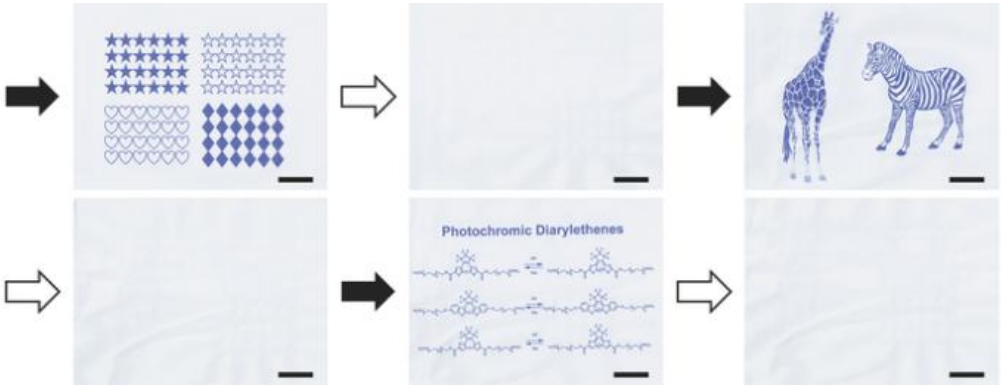



*Figure 11: Repeated print–erase cycles on the same paper using ink-jet printer. The image was observed to completely disappear upon irradiation with the Xe lamp for 30 s [40].*

The next example of functional application of photochromic inks is security printing. By printing patterns and data using both photochromic ink and ordinary ink, it is possible to create an optically variable marks and so to create the document that is difficult to forge and easy to authenticate [41].

### 2.2.3 Optical Data Storage

The use of photochromic materials promises new recording media with increased memory densities. The opportunity to dramatically increase the achievable memory density is provided by the multiplexing of light characteristics such as wavelength, polarization and phase. The use of photochromic materials in 3D memory system is desirable because they present several major advantages over current optical systems, for example they may undergo photon-mode recording that is based on a photochemical reaction within the medium, they also bring erasable capability, high resolution and high sensitivity. Utilizing two-photon excitation is a key to achieve effective 3D memory systems [2], [33].

### 2.2.4 Photo-responsive Liquid Crystals

Photochromic liquid crystal (LC) systems are able to change their long range ordering and optical properties in response to light stimuli. This ability is supported by the cooperative motion of LC molecules; if a small amount of these molecules change its orientation or conformation with light, other LC molecules follow this change. This response to light may therefore be amplified into conversion of significant length–scales. The transfer between individual phases is used in LC applications. Optical switching devices and information systems take advantage of photochemical phase transitions between nematic and isotropic phase [42]. This transfer is achieved by incorporation of small amount of photochromic structure into LC system and by photochromic isomerisation that is caused by subsequent irradiation of such a mixture. This transition is reversible and thermodynamically driven [2].

One of the possible applications of photochromic cholesteric polymers is as smart label for thermal monitoring [43]. For this purpose, new reversible temperature-sensitive polymeric materials with a broad range of trigger temperature were produced using crystalline copolymers functionalized with azoaromatic materials. By inducing the azoaromatic trans-cis isomerization through UV irradiation, it is possible to break the native chiral supramolecular conformational order, leading to an amorphous transparent phase which is characterized by different UV–VIS spectrum. If the temperature is over the polymer trigger temperature, the strongly coloured LC phase is restored and may be UV irradiated again that is making these labels reusable. During the preparation of polymeric material it is possible to tune the trigger temperature and photoswitchable properties, which allows the production of tailored labels suitable for a huge diversity of products.

# 3 Experimental Part

The main goal of the experimental part of this thesis was to incorporate the photochromic spiropyran into various polymeric matrixes and to observe if the presence of this substance leads to the change of its properties; attention was especially paid to the optical and electrical characterization. Therefore, the thin layers of pure polymeric materials as well as layers of spiropyran-doped materials were prepared and their optical properties were studied by UV-VIS spectroscopy; the measurement of current-voltage characteristics provided information about electrical properties. The description of the used polymeric materials, the method of the thin layers preparation and of optical and electrical characterization itself is discussed below.

## 3.1 Used Materials

For the purpose of studying the influence of the photochromic spiropyran on the properties of polymeric matrices, spiropyran SP1 was used. Its systematic name is 1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2'-(2*H*)-indole], CAS number 1498-88-0 and its structural formula is shown by the Figure 12. This substance was purchased from Sigma–Aldrich Company.

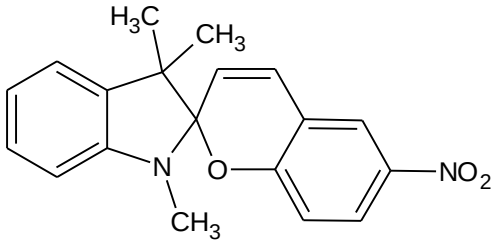
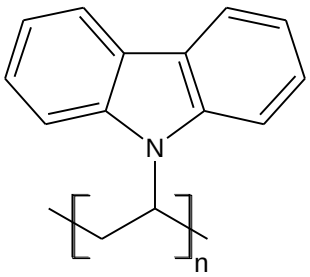



*Figure 12: The structural formula of SP1.*

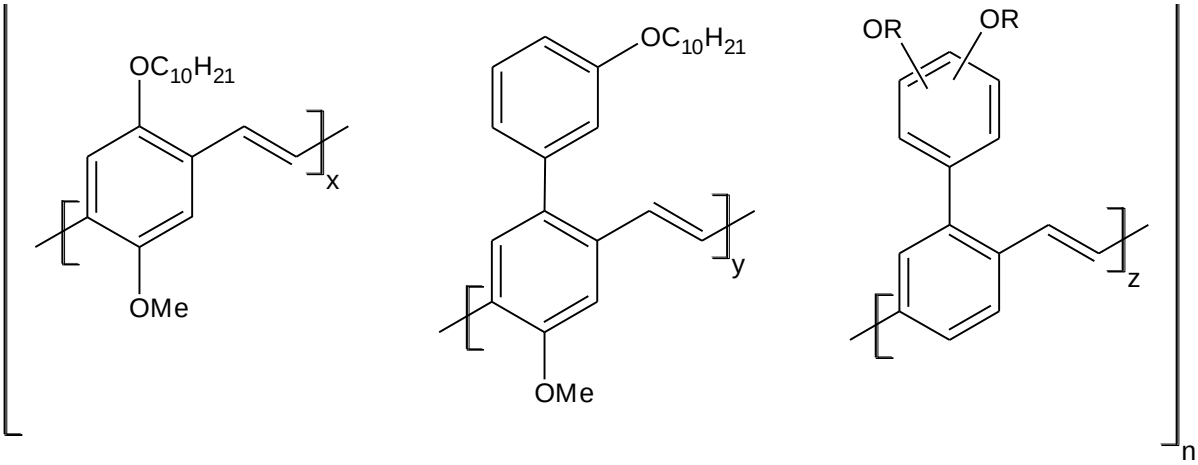
To observe the changes of optical and electrical properties caused by photochromic spiropyran SP1, this molecule was incorporated to 4 polymeric matrices, namely PVK, Tg PPV, PCDTBT and PCBTDPP. Structural formulas together with systematic names and CAS numbers of these polymers are shown by the Figure 13 – Figure 16. Polymers PVK and PCBTDPP were purchased from Sigma–Aldrich Company, polymer Tg PPV from Merck Group and polymer PCDTBT from Ossila.




Poly(9-vinylcarbazole)

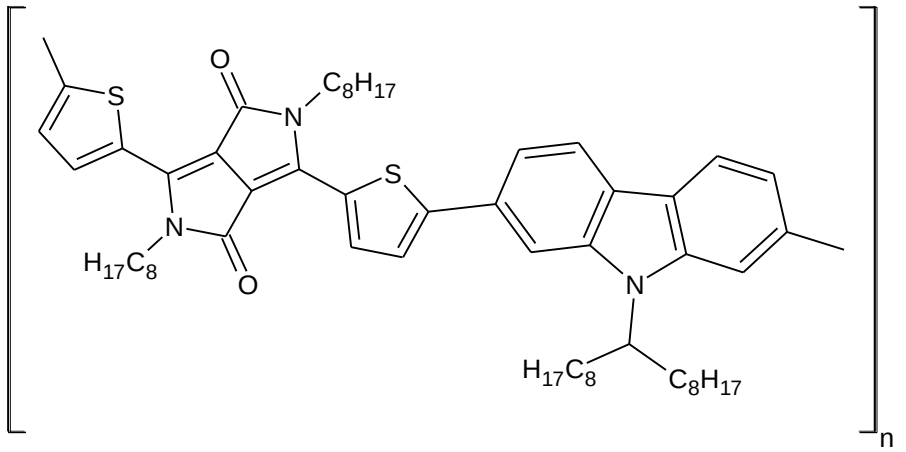
CAS 25067-59-8

*Figure 13: Polymer PVK; structural formula, systematic name, CAS number.*




Poly[3’(decyloxy)-4-methoxy-2-vinyl-1,1’-biphenyl]
Poly[1-(decyloxy)-4-methoxy-2-vinylbenzene] Poly(4-methoxy-2-vinyl-1,1’-biphenyl)

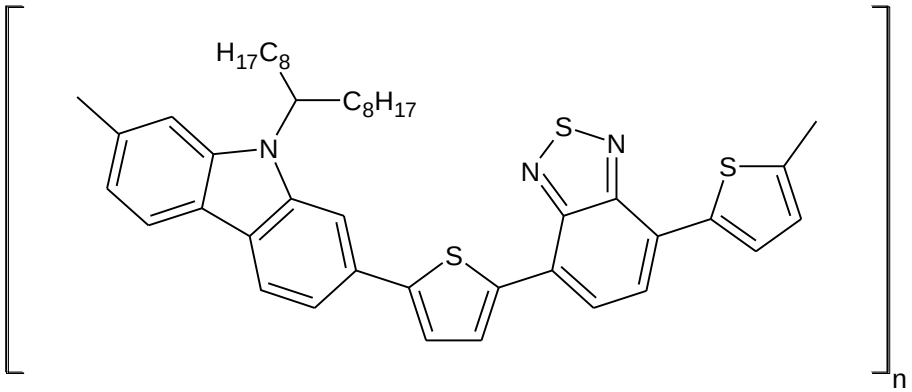
*Figure 14: Polymer Tg PPV; structural formula, systematic name. Copolymer designed by the Merck Group, the registration number 4.80823.9999.*




Poly[*N*-9'-heptadecanyl-2,7-carbazole-*alt*-3,6-bis(thiophen-5-yl)-2,5-dioctyl-2,5-dihydropyrrolo [3,4]pyrrole-1,4dione]

CAS 1147374-60-4

*Figure 15: Polymer PCBTDPP; structural formula, systematic name, CAS number.*

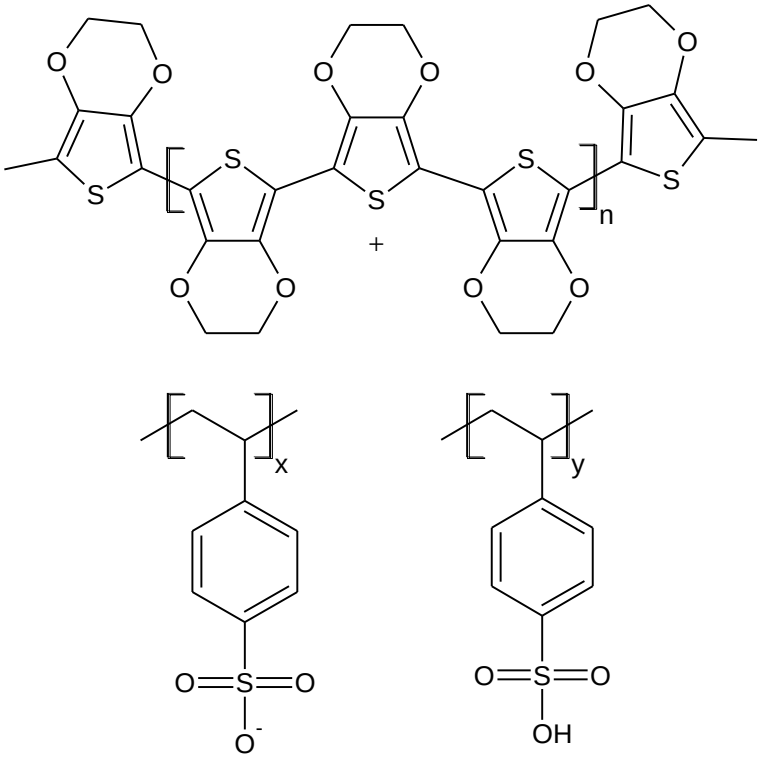



Poly[*N*-9'-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]

CAS 958261-50-2

*Figure 16: Polymer PCDTBT; structural formula, systematic name, CAS number.*

For electrical characterization, diode like structures were prepared. In this case, three auxiliary materials were used. First of them is PEDOT:PSS. Its structural formula along with systemic name and CAS number is shown by the Figure 17. This copolymer is one of the most commonly used hole transport layer. This material was purchased from Ossila. The second auxiliary material is ITO (Indium Tin Oxide, $In_2O_3/SnO_2$, CAS number 50926-11-9). Thanks to its optical transparency and electrical conductivity, this material is one of the most widely used transparent electrode material.

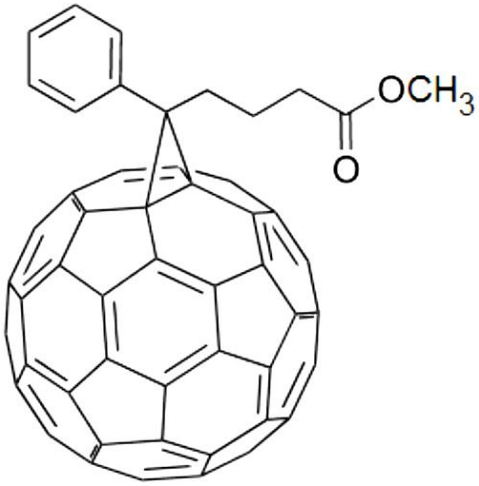


Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)

CAS 155090-83-8

*Figure 17: Copolymer PEDOT:PSS; structural formula, systemic name, CAS number.*

The last auxiliary material used during diode like structure preparation is PCBM. Its structural formula along with systemic name and CAS number is shown by the Figure 18. This structure is a derivate of fullerene $C_{61}$ and acts as an electron acceptor. It is commonly used in combination with electron donors such as conjugated polymers. This material was purchased from Sigma–Aldrich Company.




[6,6]-Phenyl $C_{61}$ butyric acid methyl ester

CAS 160848-22-6

*Figure 18: Molecule $PC_{61}BM$; structural formula, systematic name, CAS number.*

## 3.2 Optical Characterization

One of the goals of this thesis was to study the photochromic activity of the molecule SP1 within varied polymeric matrices. Both, the ability of spiropyran to undergo UV induced photochromic conversion within particular matrix as well as the reverse conversion of merocyanine form to its initial structure induced by heat were monitored. The method of UV-VIS spectroscopy was used to identify the open and closed form of spiropyran absorbing, due to the presence of different chromophores, different range of wavelengths, see Figure 19. This figure shows the conversion of spiropyran to the open form together with absorption spectra of both of these isomers. The chromene halve of the spiropyran molecule absorbs in the range 200–300 nm. As was mentioned above, the UV radiation induces the heterolytic cleavage of the carbon-oxygen bond within this chromophore, which causes the change of the structure and so the change of the chromophore. Therefore, the conversion leads to the decrease of the absorbance in the mentioned range, denoting the decline of concentration of closed form. On the other hand, the chromophore of the open form causes formation of a new peak in the area 450–650 nm together with increased absorbance around 400 nm. Therefore, the activity of photochromic within the matrix is possible to assess by the absorption spectra obtained before and after UV irradiation. The relevant absorption spectra were detected for the samples in the form of thin films. To prepare these films, the method of spin-coating was used.

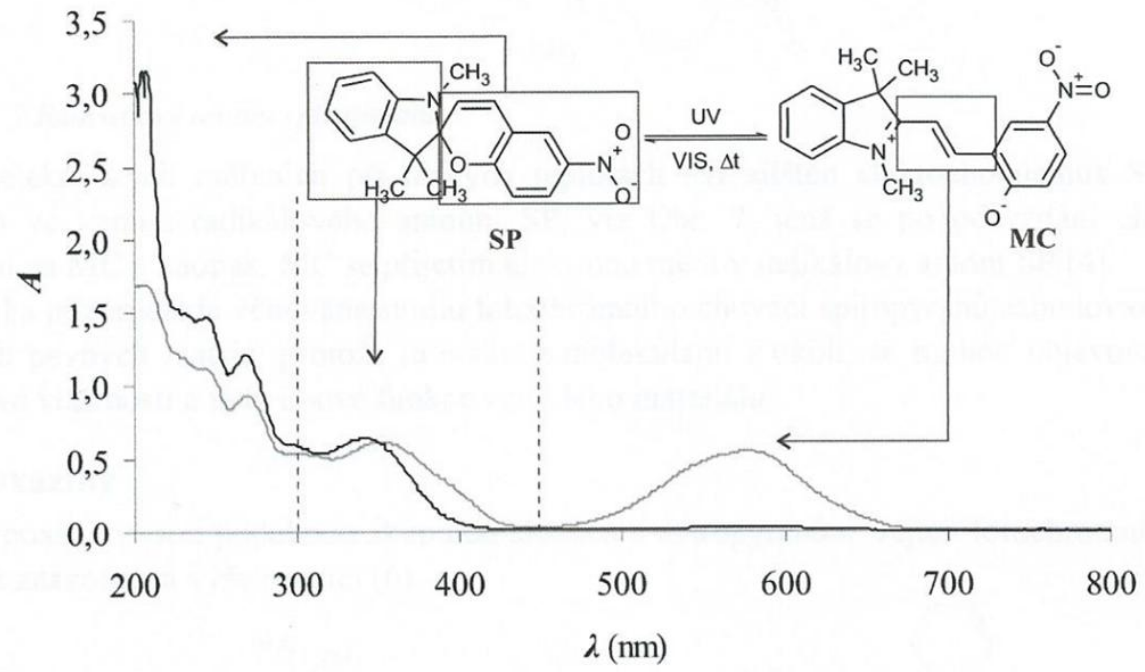



*Figure 19: Conversion of spiropyran to merocyanine form together with absorption spectrum of spiropyran (black curve) and merocyanine (grey curve) incorporated into polymer PMMA. Arrows show characteristic regions of absorption corresponding to each absorption chromophore [7].*

### 3.2.1 Used Methods

#### *3.2.1.1 UV-VIS Spectroscopy*

This method is based on the ability of the sample to absorb radiation of various wavelengths, according to the HOMO-LUMO energy gap. The absorption is therefore connected with electronic transitions. So, the principle of this method is to irradiate the sample by the radiation of known intensity and wavelength and to measure the energy that is being absorbed by passing through the sample. The output is an absorption spectrum which is a wavelength dependence of absorbance or transmittance. The curve shape of spectrum is affected by the presence of chromophores within the molecule and by their corresponding absorption bands. Typically, the wavelength at maximal light absorbance $\lambda_{max}$ and the value of absorbance at this wavelength are the most important information obtained from the absorption spectrum [44].

The absorbance is defined as the common logarithm of the ration of the light intensity at the wavelength before ($I_0$) and after ($I$) it passes through the sample:

$$A = \log \frac{I_0}{I} \tag{10}$$

For the thin layer, the absorbance is dependent on the layer thickness $d$ and on absorption coefficient $\varepsilon$:

$$A = \varepsilon \cdot d \tag{11}$$

To observe absorption spectra and thereby to observe changes in the optical properties of the samples, UV-VIS spectrophotometer Varian Cary 50 was used. This device consists of Xenon pulse lamp, Czerny-Turner monochromator, dual Si diode detectors and quartz overcoated optics [45].

#### *3.2.1.2 Spin-coating*

The spin-coating is one of the most commonly used techniques of thin layer deposition to substrate. That is because of its ability to easily, quickly and reproducibly fabricated thin films with high structural uniformity of various organic materials. This method also allows the control of the film morphology through parameters such as rotational speed or solution concentration [46]. The deposition process consists of 4 steps, see Figure 20. First, the substrate is covered by the excess of the polymer solution, then the substrate start to rotate at high speed (500–8 000 rpm), so the solution surplus is spun off. The majority of the remaining solvent is dried by the airflow leaving the film of dissolved molecules on the substrate surface. The thickness of the thus formed film lies in the range of 10–200 nm and depends upon the parameters such as solution viscosity, rotation speed and time and solvent evaporation rate [47].The exact thickness of a film was measured by surface profilometry.

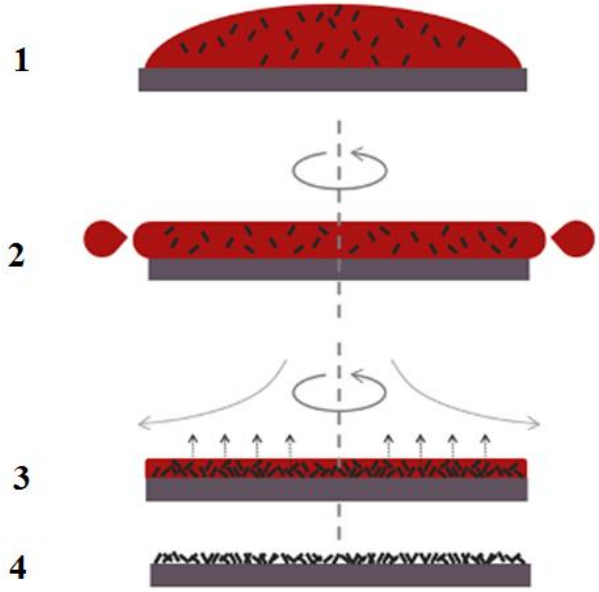



*Figure 20: Single steps of static spin-coating; applying the solution (1), spin of the solution surplus by rotation (2), solvent evaporation (3) and formation of a thin layer of the dissolved substance (4) [47].*

This substrate coating technique has also some disadvantages. The drying time is fast which can leads to the lower performance for some nano-technologies. So, the time for self-assemble or crystallise is required. Also, the material usage is typically very low, only around 10 % or even less [47].

### 3.2.2 Sample Preparation

Altogether, eight solutions were prepared, see Table 1. Half of them consisted of pure polymers at the concentration of 5 $mg.ml^{-1}$ (the only exception was the solution containing polymer PVK, its concentration was due to its low molecular weight 20 $mg.ml^{-1}$) dissolved in the anhydrous chlorobenzene. The second part differed just by the content of photochromic spiropyran SP1 at the concentration of 30 wt.% of polymer. Filtered solutions were deposited under the nitrogen atmosphere in the glovebox to the pure glass slides by the spin-coating method. The setting of the rotation speed was 1 000 rpm and the time of rotation was 40 s. Thus, thin layers with a thickness of several hundredths of micrometer were created. From each solution, two samples were prepared. Therefore, two sets of the same thin layers were obtained; one was used to monitor the ability of SP1 to convert into its merocyanine form by UV induction within different matrices, the other to observe the heat-induced reverse conversion to the initial structure.

*Table 1: The composition of individual solutions together with the thickness of prepared layers*

| Polymer matrix | Polymer content (mg) | Spiropyran content (mg) | Solvent amount (µl) | Layer thickness set 1 (nm) | Layer thickness set 2 (nm) |
|---|---|---|---|---|---|
| PVK | 10,0 | 0 | 500 | 170±10 | 160±10 |
| Tg PPV | 2,5 | 0 | 500 | 610±60 | 600±50 |
| PCBTDPP | 2,5 | 0 | 500 | 140±30 | 160±20 |
| PCDTBT | 2,5 | 0 | 500 | 280±50 | 260±30 |
| PVK | 10,0 | 3,00 | 500 | 230±50 | 240±40 |
| Tg PPV | 2,5 | 0,75 | 500 | 720±20 | 720±20 |
| PCBTDPP | 2,5 | 0,75 | 500 | 280±20 | 280±20 |
| PCDTBT | 2,5 | 0,75 | 500 | 170±20 | 170±10 |

### 3.2.3 Experimental Procedure

#### *3.2.3.1 Photochromic Conversion Induced by UV Light*

To observe the ability of the molecule SP1 to undergo UV induced photochromic conversion within particular matrix, absorption spectra of the first set of thin layers were obtained by the measurement by the device Varian Cary 50. For these measurements, the wavelength range 200–850 nm with 1 nm step was set. The spectrum of a pure glass slide was used as a baseline. After that, all of the samples were illuminated for 15 min by UV lamp with wavelength spectrum in the UVA spectral range. Hereby, the photochromic conversion was induced and the absorption spectra were obtained once again by the same measurement. This experiment was carried out with both, samples doped by photochromic SP1 and also with samples of pure polymers to observe which changes of absorption spectra are caused by the degradation of polymer due to the UV light.

#### *3.2.3.2 Thermally Induced Reverse Conversion*

Thin layers of the second set were used to find out, how fast is the reverse conversion of merocyanine to spiropyran within various matrices and so to confirm that photochromic reaction of spiropyran is reversible and also that the back reaction is thermally driven. These samples underwent the same treatment as the first set, so the absorption spectra before and after UV induced conversion were obtained. Then, irradiated samples containing merocyanine form were heated for 5 min on the hot plate set to the temperature 45 °C and their absorption spectra were measured as well. This heating cycle was repeated three times. In the case of polymer PCBTDPP, the reversion of merocyanine form to the spiropyran was not observed by this treatment, so this sample was for another 5 minutes exposure to the temperature 75 °C. Again, the wavelength range 200–850 nm with 1 nm step was set for these measurements. This experiment was carried out with both, samples doped by photochromic SP1 and also with samples of pure polymers to observe which changes of absorption spectra are caused by the degradation of polymer due to the heat and UV light.

### 3.2.4 Results

#### *3.2.4.1 Photochromic Conversion Induced by UV Light*

The aim of this part of the optical characterization was to observe if the UV-induced photochromic conversion of the molecule SP1 occurs after its incorporation within different polymeric matrices. Therefore, the absorption spectra of thin layers of pure and SP1 doped polymers PVK, Tg PPV, PCBTDPP and PCDTBT before and after UV irradiation were obtained, see Figure 21 – Figure 24. Because it was not possible to ensure, all of the spectra will be obtained for exactly the same point of the layer, these spectra were, due to the surface roughness and due to the fact that the layer is thicker at the edge of the sample in comparison with the centre, normalised.

The Figure 21shows normalised absorption spectra of thin layers contained pure and SP1 doped polymer PVK before and after UV irradiation. Curves obtained for the pure polymer PVK are almost equal, with the absorption maxima around 250, 300 and 350 nm and minimal absorbance in the area 380–700 nm. Normalised absorption spectra of layer containing SP1 show increased relative absorbance in the range around 200 nm. When the photochromic conversion was induced within the doped sample, new peak in the range of 500–650 nm was achieved.

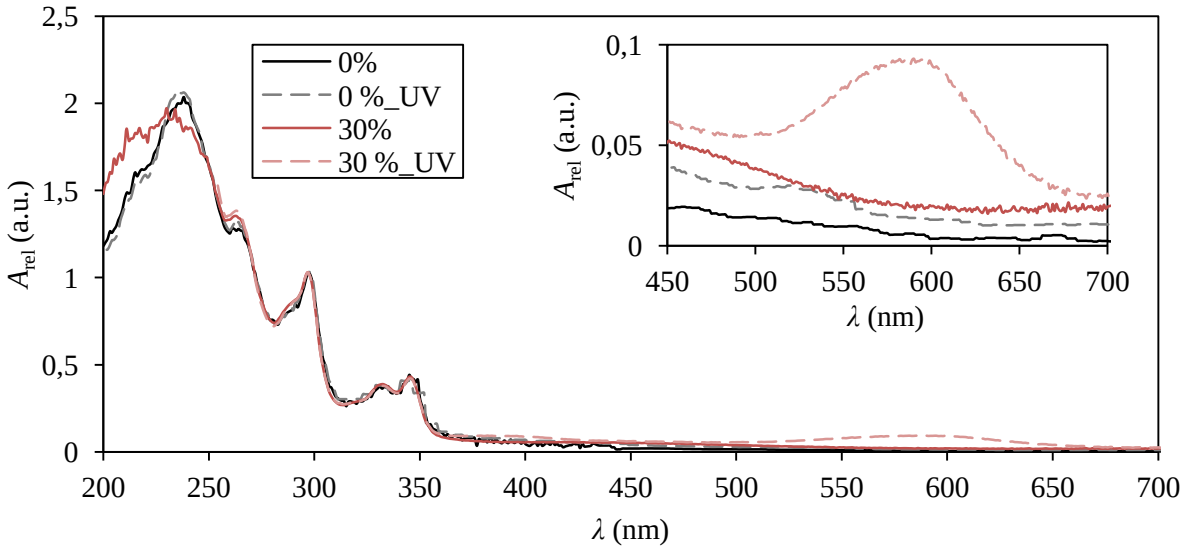



*Figure 21: Normalised absorption spectra of samples containing polymer PVK as a matrix together with the detail of characteristic absorption area of merocyanine form. Curves marked by '0 %' refer to pure polymer, '30 %' to doped polymer.*

In the case of sample containing pure polymer Tg PPV, the normalised absorption spectrum with two absorption maxima, first around 200 nm, second approximately in 500 nm, and minimal relative absorbance in the area 600–850 nm was achieved. The curve obtained after UV irradiation exhibits the same shape with no significant differences. The spectrum corresponding to the layer containing doped material shows bathochromic shift and increased relative absorbance in the range of 200–400 nm. After the UV irradiation, the relative absorbance increased in the areas around 400 and 600 nm, compared to the initial curve of doped material, see Figure *22*.

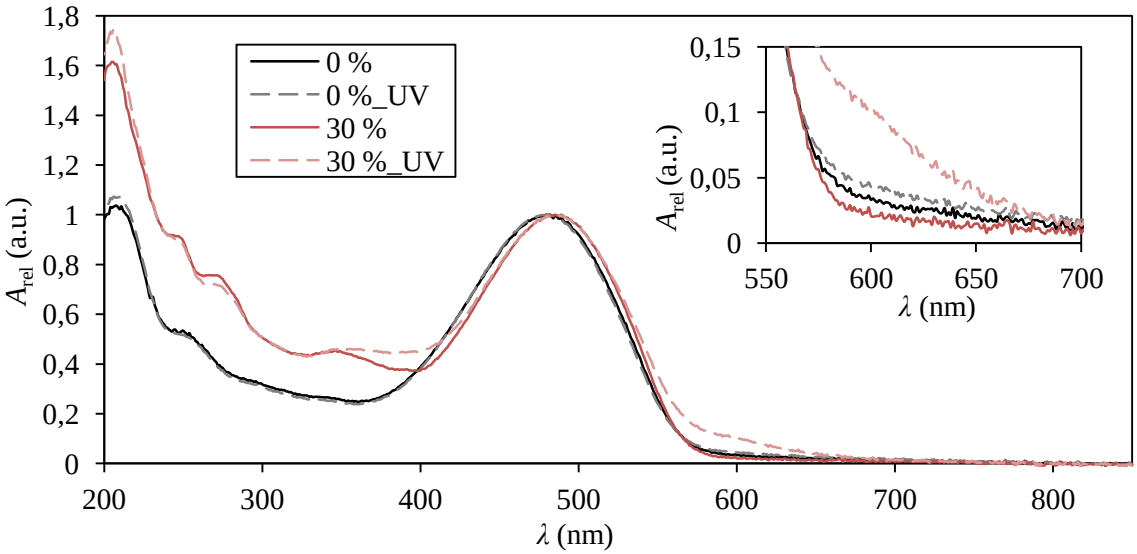



*Figure 22: Normalised absorption spectra of samples containing polymer Tg PPV as a matrix together with the detail of characteristic absorption area of merocyanine form. Curves marked by '0 %' refer to pure polymer, '30 %' to doped polymer.*

Normalised absorption spectrum of polymer PCBTDPP shows maximal absorbance approximately at 680 nm along with other peaks at 280 and 390 nm. Again, the curve obtained after UV irradiation does not exhibit any induced changes. The presence of SP1 structure leads to the bathochromic shift and increased relative absorbance in the range of 200–400 nm. After UV irradiation of doped polymer PCBTDPP, the relative absorbance increased in the range of 370–650 nm, see Figure 23.

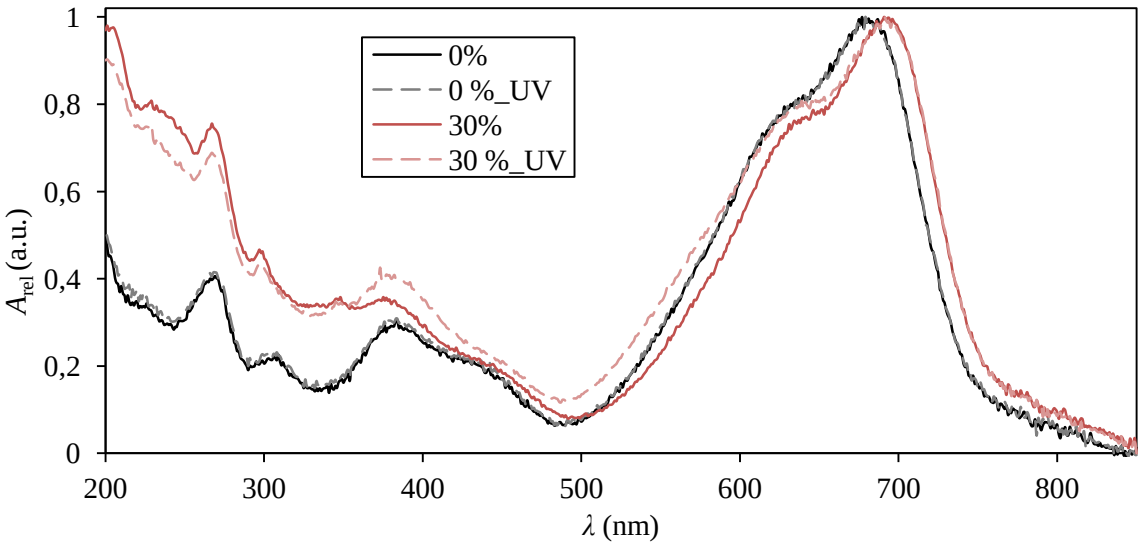



*Figure 23: Normalised absorption spectra of samples containing polymer PCBTDPP as a matrix. Curves marked by '0 %' refer to pure polymer, '30 %' to doped polymer.*

Normalised absorption spectrum of pure polymer PCDTBT exhibits absorption maxima at 280, 400 and 590 nm, as well as the curve obtained after UV irradiation. Again, curves obtained for the doped layers show increased relative absorbance in the area 200–380 nm, Figure 24.

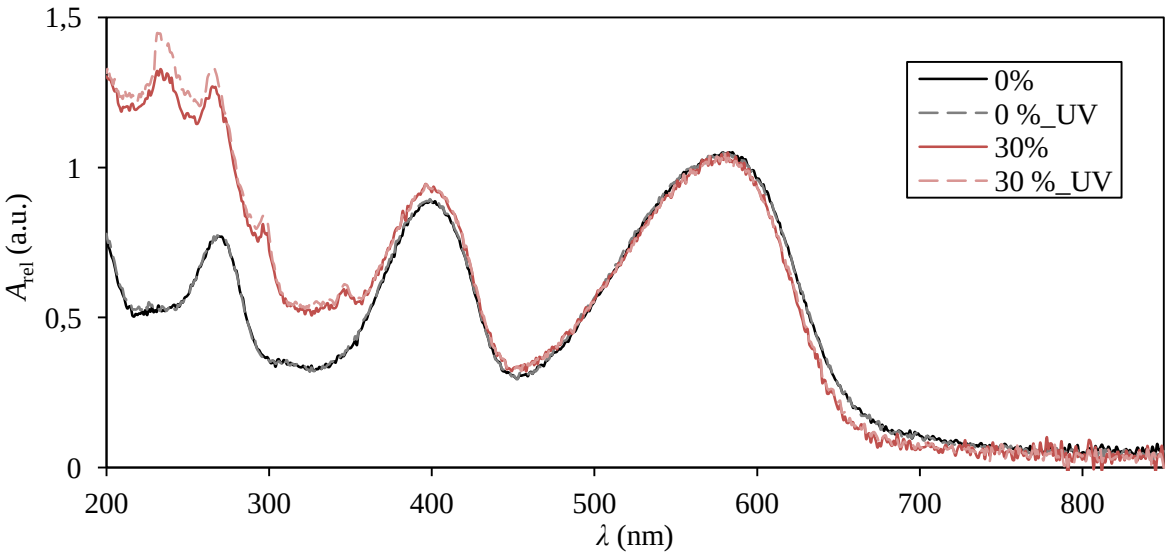



*Figure 24: Normalised absorption spectra of samples containing polymer PCDTBT as a matrix. Curves marked by '0 %' refer to pure polymer, '30 %' to doped polymer.*

Photochromic switching between isomeric forms is even eye observable. The most significant colour change was detected for sample consisting of polymer PVK as a polymeric matrix. Polymer PVK itself is transparent and the presence of spiropyran does not lead to the noticeable colour change. After UV irradiation, the colour of the sample turns purple, see Figure 25, which is caused by the formation of the new chromophore after heterolytic cleavage of carbon-oxygen bond within SP1 molecule. Within 24 hours the initial closed form is thermally restored and so the layer recovers its original transparency.

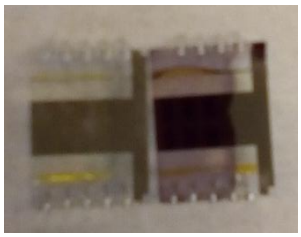


*Figure 25: Prepared diode like structure containing closed (left) and open (right) form of SP1.*

*Discussion*

Obtained absorption spectra may be interpreted in regard to the Figure 19 that shows changes of absorption spectra induced by the photochromic conversion of SP1. The figure indicates, the presence of the chromene halve within the spiropyran molecule leads to the increased absorbance especially in the range 200–300 nm. After sample irradiation, spiropyran converts to its merocyanine form, resulting in increased relative absorbance in the range 500–650 nm. The reduction of the spiropyran concentration caused by this conversion is indicated by the increase of the relative absorbance in its characteristic absorption area. These changes of absorption spectra are more pronounced the higher the concentration of SP1 is.

According to the obtained absorption spectra it is possible to say the photochromic conversion was achieved within layers consisted of polymer PVK as a matrix. The increased relative absorbance of the doped polymer in the range around 200 nm indicates the presence of chromene halve within the spiropyran structure. Due to the absorption bands of polymer PVK, this material seems to be the most suitable polymer matrix for observation of the concentration changes of merocyanine form

within the sample by means of the absorption spectra, because it does not absorb wavelength in the range around 500 nm, see Figure 21. The formation of a new peak after UV irradiation shown in the detail of this area indicates increased amount of the open form. The conversion of SP1 to its merocyanine form was not confirmed by the decrease of absorption in characteristic absorption region of spiropyran due to the overlapping absorption band of the polymer. The curves obtained for the pure polymeric matrix confirmed all the change may be attributed to the photochromic conversion because no degradation caused by the UV light was observed.

The changes observed within absorption spectra of samples containing polymers Tg PPV and PCBTDPP are also attributed to the photochromic activity. Again, no degradation due to the UV light was observed. Absorption spectra of these polymers allows to monitor concentration changes of both, closed form and, with some restrictions caused by the overlapping of absorption band of merocyanine with the band of polymers, even the open form, see Figure 22 and Figure 23. The noticeable increase of relative absorbance in the range of 200–400 nm obtained for the doped materials confirms the presence of closed form of photochromic. Another increase of absorbance achieved in the area around 600 nm in the case of sample of doped polymer Tg PPV as well as doped polymer PCBTDPP after the photochromic conversion was induced indicates the formation of merocyanine. Despite these undoubted signs of the SP1 conversion, the decrease of the relative absorbance in the area around 200 nm denoting the reduction of closed form concentration is visible only in the case of layer containing polymer PCBTDPP as a matrix. The observed bathochromic shift caused by the presence of photochromic molecule may be explained by the chromophore accumulation, but to prove this and to find out its mechanisms, further experiments would be required.

The observed increased absorbance in the characteristic absorption area of SP1 for the layers consisting of polymer PCDTBT as a matrix indicates the presence of closed photochromic form. The absorption spectrum of the polymer PCDTBT completely overlaps the characteristic absorption band of merocyanine form and therefore allows observation only of the concentration changes of spiropyran, see Figure 24. Therefore, there is no visible change in the range around 550 nm for the doped material after UV irradiation indicating presence of open form. Moreover, the curve obtained after UV irradiation is almost the same as the one before it, which denotes that the photochromic conversion was not achieved within this sample. This effect cannot be attributed to the polymeric matrix, according to the results of the following experiments, namely to the Figure *30*, where the conversion considerably occurred, but to the experimental error, that probably arose during UV irradiation.

The differential spectra show the yield of the photochromic conversion within individual matrices, see Figure 26. It is the wavelength dependence of change of the absorbance caused by the conversion:

$$\Delta A = \left| \frac{A_{beforeUV} - A_{afterUV}}{A_{beforeUV}} \right| \tag{12}$$

It shows the highest yield was obtained within the polymer PVK. The yields within other matrices are insignificant in comparison with this one (the one within polymer PVK is about ten times higher than within other polymers), which can be caused by the overlapping of the absorption band of merocyanine form with the band of polymers. It is the demonstration of the influence of the environment on the photochromic conversion.

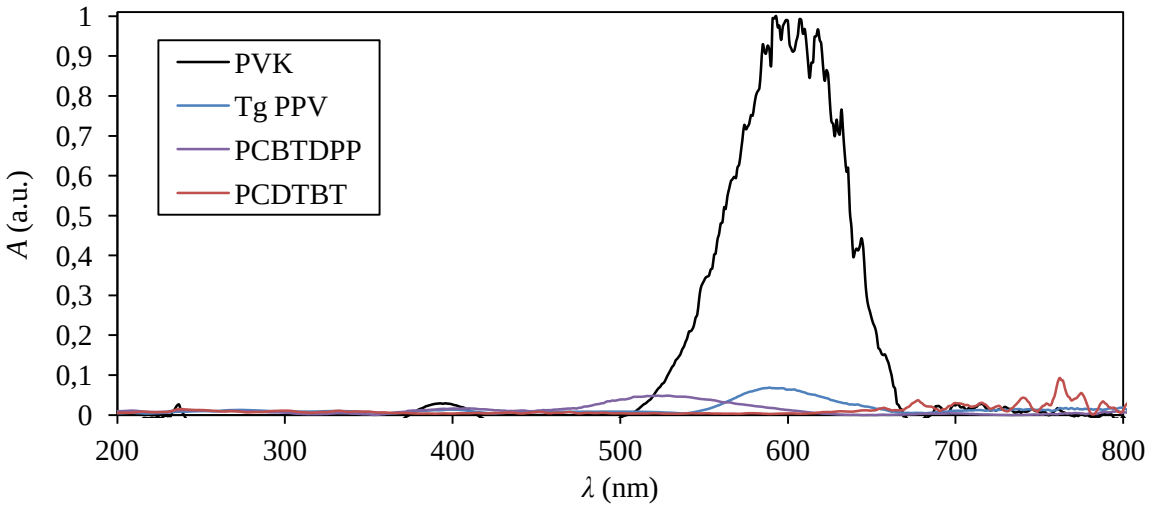



*Figure 26: The differential spectra of photochromic conversion within different matrices.*

### *3.2.4.2 Thermally Induced Reverse Conversion*

The aim of this part of the optical characterization was to find out, how fast is the reverse conversion of merocyanine to spiropyran within various polymeric matrices and so to confirm that photochromic reaction of spiropyran is reversible and also that the back reaction is thermally driven. Therefore, the absorption spectra of thin layers of pure and SP1 doped polymers PVK, Tg PPV, PCBTDPP and PCDTBT before and after UV irradiation together with absorption spectra measured after each of three heating cycles were obtained, see Figure 27 – Figure 30. Again, because it was not possible to ensure, all of the spectra will be obtained for exactly the same point of the layer, these spectra were, due to the surface roughness and due to the fact that the layer is thicker at the edge of the sample in comparison with the centre, normalised.

All of the curves obtained for the doped layer consisted of the polymer PVK as a polymeric matrix seems to be equal, with minimal relative absorbance in the area 370–700 nm, absorption maximum around 230 nm along with other peaks at 300 and 350 nm. Only the detail of the region 500–650 nm shows the increased relative absorbance after irradiation of the sample by UV light, see Figure 27.

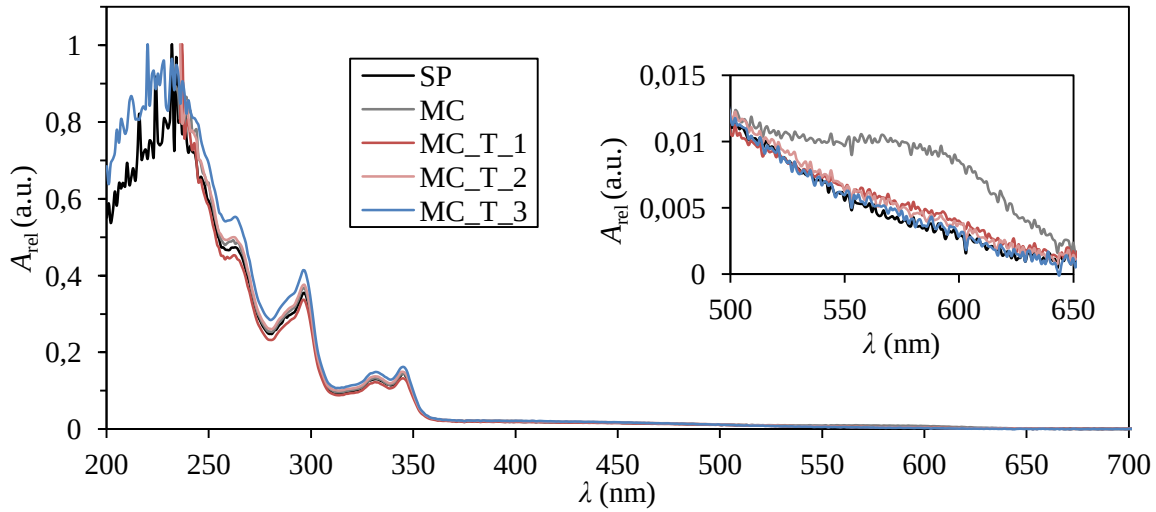



*Figure 27: Normalised absorption spectra showing thermally induced reverse conversion of photochromic after its incorporation into the PVK matrix together with the detail of characteristic absorption area of merocyanine form. The letter 'T' means heating cycle and followed number marks number of cycle.*

In the case of sample containing polymer Tg PPV as a matrix, spectra exhibiting absorption maxima at 200 and 480 nm and minimal absorption of wavelengths 650 nm and higher were achieved. The changes within individual absorption spectra are clearly observable especially in the detail of the area 550–650 nm, see Figure *28*. It shows increased relative absorbance induced by UV light. After each heating cycle, the relative absorbance in this region gradually decreases towards the curve obtained for the initial layer. Slight differences are observable also in the region around 200 nm. After UV irradiation, the absorbance decreases and started to subsequently increase after each heating cycle.

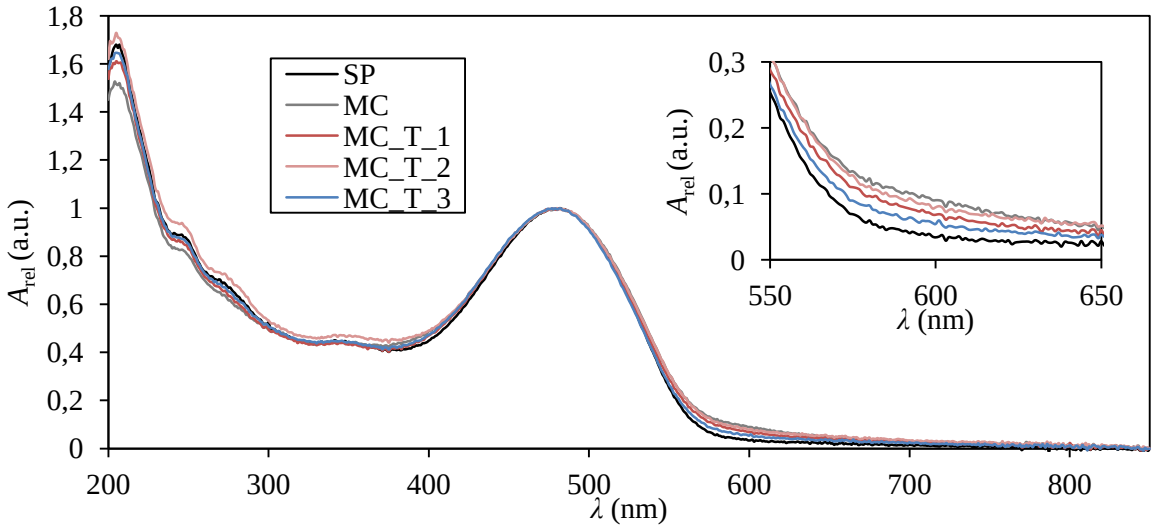



*Figure 28: Normalised absorption spectra showing thermally induced reverse conversion of photochromic after its incorporation into the Tg PPV matrix together with the detail of characteristic absorption area of merocyanine form. The letter 'T' means heating cycle and followed number marks number of cycle.*

Normalised absorption spectra achieved for the layer consisting of polymer PCBTDPP as a matrix show absorption maximum at 650 nm, minima at 500 and 850 nm and considerably differences of the relative absorbance in the area 200–400 nm, caused by the UV induced photochromic conversion and consequent heating cycles, see Figure 29. The curves obtained for the first three heating cycles are almost the same as the one obtained after conversion. All of these curves exhibit decrease of the relative absorbance in the mentioned area compared to the curve obtained before UV irradiation. The absorption spectrum achieved after exposure the sample to the higher temperature shows another drop of absorbance. Moreover, this curve follows the shape of the one obtained for the layer consisted of the pure polymer.

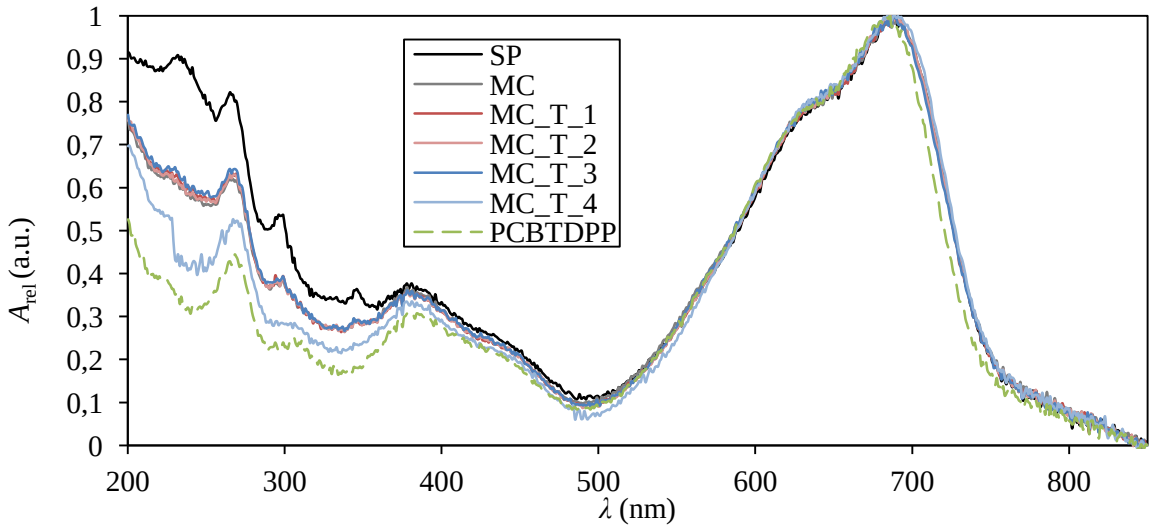



*Figure 29: Normalised absorption spectra showing thermally induced reverse conversion of photochromic after its incorporation into the PCBTDPP matrix together with the absorption spectrum of a pure polymer. The letter 'T' means heating cycle and followed number marks number of cycle.*

In the case of absorption spectrum achieved for the sample consisting of PCDTBT as a polymeric matrix doped by SP1, the curve with absorption maximum at 250 nm and peaks at 400 and 490 nm was achieved, see Figure 30. The UV irradiation and consequent heating cycles caused changes of relative absorbance in the range of 200–400 nm and also in the region 420–520 nm, according to the detail of that area. The curve achieved after UV induced photochromic conversion exhibits decreased relative absorbance in the both of mentioned areas. After each of heating cycles the absorbance gradually increases and the curve obtained after the third cycles is almost equal to the initial one.

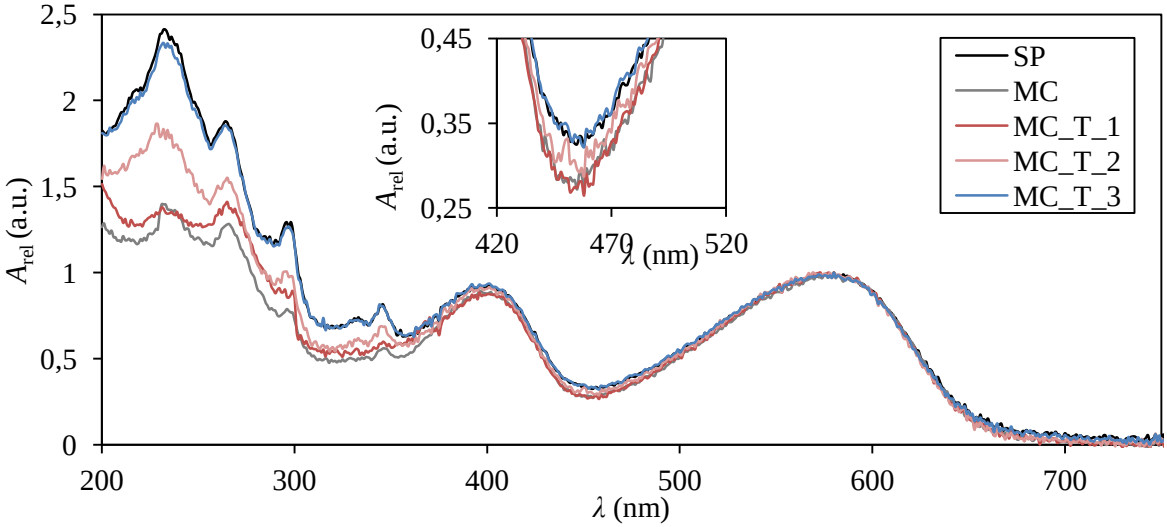



*Figure 30: Normalised absorption spectra showing thermally induced reverse conversion of photochromic after its incorporation into the PCDTBT matrix together with the detail of absorption area of merocyanine form. The letter 'T' means heating cycle and followed number marks number of cycle.*

The thin layer containing doped polymer PCDTBT allowed complete restoration of the initial closed form. This gradual process is shown by the Figure 31. It gives information about the kinetic of the back reaction through the change of the SP1 concentration with the heating time.

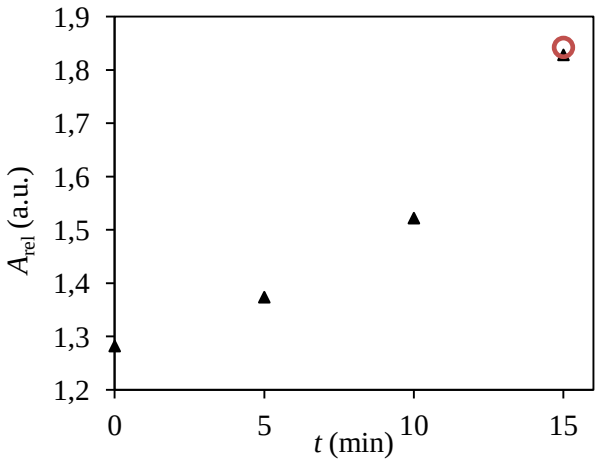



*Figure 31: The heating time dependence of normalised absorbance for the doped polymer PCDTBT at wavelength 266 nm. The red circle indicates the value of normalised absorbance obtained before UV irradiation.*

*Discussion*

The reverse conversion of merocyanine to spiropyran under highest temperature was observed within different matrices. The fastest restoration of the initial closed form was observed in the case of sample containing polymer PVK as a matrix, where the complete conversion occurred after the first cycle of heating. The curve identical to the one obtained before UV irradiation was gained, see Figure 27. Curves reflecting changes that took place within the sample after the remaining two heating cycles are also equal to the first one which indicates that the UV irradiation and followed heating did not cause the degradation of the material.

The detail of the area 550–650 nm within absorption spectra obtained for the layer containing polymer Tg PPV as a matrix shows that the photochromic reverse conversion is gradual, see Figure 28. Together with the number of heating cycles the relative absorbance increases in the characteristic absorption region of spiropyran and decreases in the characteristic region of merocyanine. However, these changes are insignificant compared with differences induced in spectra of other matrices.

According to the absorption spectra obtained for the layer consisting of the polymer PCBTDPP as a matrix, the reverse conversion of photochromic SP1 does not occur within this environment, see Figure 29. The UV irradiation of the doped polymer causes the decrease of relative absorbance in the characteristic absorption area of spiropyran denoting the reduction of the concentration of this closed form caused by the conversion. However, the first three heating cycles does not induce any change of the curve and thus the concentration of the molecule SP1 remain the same as before heating. Consequent exposure to the higher temperature leads to another drop of relative absorbance in the absorption region of spiropyran which indicates the degradation of this structure by the heat. The fact that the initial form of photochromic was not restored may be explained by the stabilization of the merocyanine form by the environment.

Polymer PCDTBT is the next matrix that allows complete restoration of the initial closed form. The conversion is slower compared to the PVK environment and therefore it enables to observe the gradual process of the reversion, see Figure 30.

### 3.2.5 Summary of Optical Characterization

The photochromic activity of the molecule SP1 within varied polymeric matrices was studied. The ability of spiropyran to undergo UV induced photochromic conversion after its incorporation within polymers PVK, Tg PPV, PCBTDPP and PCDTBT was monitored. The merocyanine form of photochromic was achieved after UV irradiation for all used matrices. The presence of molecule SP1 within the layer was indicated by the increased relative absorbance in the area around 200 nm, while the creation of merocyanine form was shown by increased absorption around 550 nm. In the case of absorption spectra obtained for the layer formed by polymer PCBTDPP as a matrix the formation of merocyanine was also indicated by the decreased absorbance in the characteristic absorption area of spiropyran denoting drop of its concentration caused by the conversion. It was found that polymer PVK seems to be the most suitable polymer matrix for observation of the concentration changes of merocyanine form within the sample by means of the absorption spectra, because it does not absorbs wavelengths in its characteristic absorption area. Therefore, it is possible to clearly observe formation of new peak induced by UV light. On the other hand, this polymer absorbs in the characteristic absorption area of molecule SP1 and so it is difficult to observe the concentration changes of this structure. Conversely, the absorption spectra of other used polymers allows to monitor concentration changes of closed form and only with some restrictions, caused by the overlapping of absorption band of merocyanine with the band of polymers, the concentration changes of open form. It was also found, that the UV irradiation does not cause the degradation of polymeric matrix. The photochromic conversion was even eye observable, especially within polymer PVK. According to the differential spectra, this polymer allows the highest yield of the conversion.

The reverse conversion of merocyanine form to its initial structure induced by heat was studied as well. It was found that the initial photochromic structure is completely restored within matrices PVK and PCDTBT. The open form was little bit more stabilized while incorporated into polymer PCDTBT, because the conversion was gradual and lasted for the three heating cycles, while in the case of polymer PVK as a matrix, the initial structure was restored after the first cycle. Even a little bit more stabilization of the merocyanine form was found for the layer formed by polymer Tg PPV, where together with the number of heating cycles the relative absorbance increases in the characteristic absorption region of spiropyran and decreases in the characteristic region of merocyanine, however, the initial structure was not achieved. The greatest stabilization of open form was found while incorporated into polymer PCBTDPP, where the photochromic reverse conversion did not occur at all. Consequent exposure to the higher temperature led to the degradation of the structure of spiropyran. This confirmed the above mentioned theory, that the photochromic activity is very sensitive to their environment.

## 3.3 Electrical Characterization

The other goal of this thesis was to study the influence of the photochromic molecule to the electrical properties of the polymeric matrix after its incorporation within it. Both, the effect of photochromic conversion and so of photoswitchable charge carrier traps to the mobility of charge carriers as well as to the photogeneration were monitored. For this purpose, the method of current-voltage measurement was used. The relevant current-voltage characteristics were detected for the samples in the form of diode like structures. For their preparation, the methods of spin-coating (see 3.2.1.2) as well as vapour deposition were used.

### 3.3.1 Used Methods

#### *3.3.1.1 Current-Voltage Characteristics*

A current-voltage characteristic of the device (I-V curve) is a plot of the applied voltage dependence of electrical current flowing through it. It allows to determine some basic parameters, which may also be used for modelling of its behaviour within an electrical circuit. The I-V curve may be measured in the dark as well as under illumination.

The dark IV measurements are invaluable in the detection of the diode properties. The curve obtained for prepared diode like structures produced the exponential curve so characteristic of diode. It starts at the zero intersection (the measurement did not include the lower left quadrant of I-V characteristic curves), the curve gradually increases but the flowing current is extremely small. At a certain voltage value, an avalanche occurs and the current increases rapidly with a very small increase in voltage producing a non-linear curve, see Figure 32 [48].

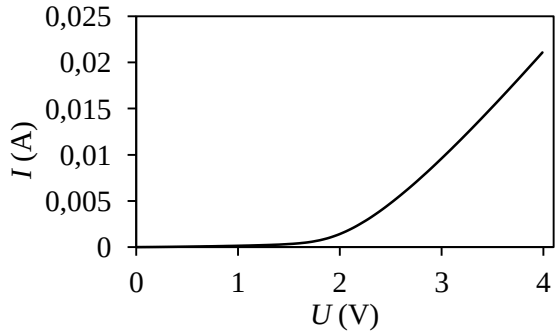



*Figure 32: The I-V curve of diode.*

The linear graph of V-A curve allows detection of only little information about the diode, much more information is revealed from a semilog plot [48].

It is well known that polymers used as an active layer within prepared structures show photogeneration under the illumination. Therefore, they may exhibit solar cell-like behaviour. The I-V curve of illuminated solar cell differs from the one obtained in the dark, see Figure 33, which is caused by the photogeneration phenomena that take place within the cell. This curve allows the determination of the main photoelectric parameters through which the solar cell is characterized. It is short circuit current $I_{SC}$, open circuit voltage $V_{OC}$, current and voltage corresponding to the maximum power point $I_{max}$ and $V_{max}$ respectively, fill factor $FF$ and solar cell efficiency $\eta$. The value of $I_{SC}$ corresponds to the current that flows out of the cell at zero outputs voltage and so at zero resistance. On the other hand, the value of $V_{oc}$ corresponds to the voltage at zero current and is the maximum value of voltage available from the solar cell. At both of these parameters, there is a zero power from the cell. The point at which the cell produces maximal power is near the I-V curve bend and is called maximum power point. This maximum power is also determined by the fill factor in conjunction with $V_{OC}$ and $I_{SC}$ [48] – [50]:

$$FF = \frac{I_{max}\, V_{max}}{I_{SC}\, V_{OC}} \tag{13}$$

All of these parameters are related to the solar cell efficiency $\eta$, which is a ratio of the maximum electrical power the cell is able to produce $P_{max}$ to input energy from the sun $P_0$ [48]:

$$\eta = \frac{P_{max}}{P_0} = \frac{I_{SC}\, V_{OC}\, FF}{P_0} \tag{14}$$

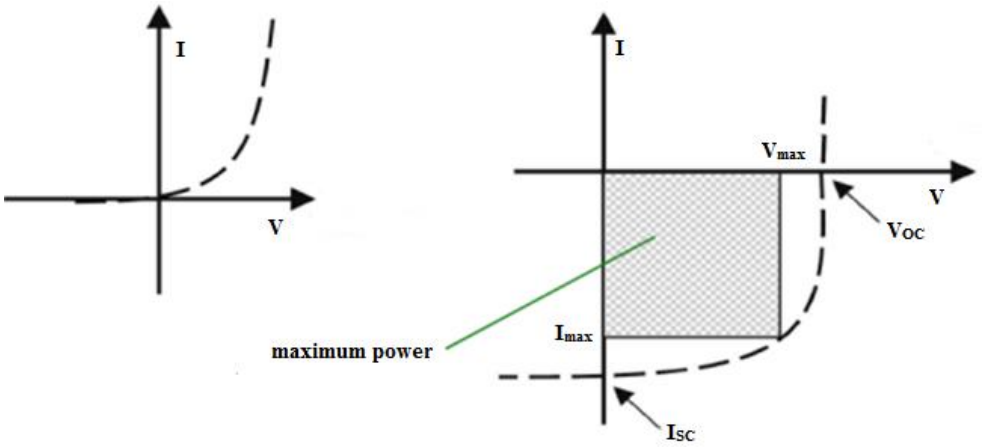



*Figure 33: I-V curve of solar cell obtained in the dark (left) and after illumination (right) together with solar cell characteristic parameters.*

The obtained I-V characteristics are influenced by space-charge limited current (SCLC). It is a mechanism of conductivity with non-linear course. It occurs only when the contact electrode is able to release either electrons to the conduction band or holes to the valence band of the semiconductor or insulator, where the initial rate of the injection of the charge carriers is higher than the rate of its recombination. Those injected carriers form area with space charge which limits conduction. It affected the course of the I-V curve, where at low field region the increase of current with voltage is relatively small, while in the higher voltages the slope of the dependence is more pronounced. In the case of material without traps for charge carriers, the limitation of the current flow by space charge is quadratic ($I \sim V^2$). The presence of the traps may cause the deformation of I-V characteristics is more significant as the exponent of the voltage is higher than two [51], [52]. The exact course of the curve is affected by the trap distribution [53]. In the case the traps are distributed only on one level, the current can be expressed as

$$j_{SCLC} = \frac{9}{8}\varepsilon\varepsilon_0\mu\theta\frac{V^2}{L^3}, \tag{15}$$

where $\varepsilon$ is the relative permittivity, $\varepsilon_0$ is permittivity of vacuum, $\mu$ is charge carrier mobility, $\theta$ is the ratio of free to total charge carriers, $V$ is the applied voltage and $L$ is the electrode distance [52].

The Figure 34 shows the SCLC characteristic of the insulator or semiconductor with wide band gap. As the current increases due to the higher field, the traps start to be filled up. The consequent increase of the voltage leads to the introducing of free carriers that cannot be captured within the trap, which is observable by the sudden and significant increase in current. The voltage at which all the traps are filled is generally called trapped-filled-limit voltage $U_{TFL}$. After that, the ratio $\theta \approx 1$and therefore the material starts to behave as the one without traps [53].

To observe I-V curves of prepared samples and thereby to observe changes in the electrical properties that take place within the doped samples due to the presence of isomeric forms of photochromic, solar simulator LOT-Oriel LS0916 and electrometer Keithley 6517B were used. The spectrum provided by the solar simulator is broadband and very close to that of sun and so is the colour temperature of the light (approximately 6 000 K). This device consists among others of xenon arc lamp with brightness 1 000 $W.m^{-2}$, an ellipsoidal reflector that is surrounding the lamp, advanced illumination homogenizer, mirror and collimating lens and therefore may produce uniform collimated beam [54], [55].

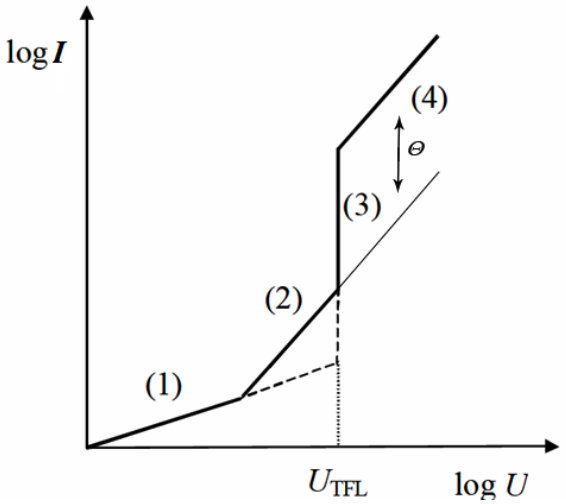



*Figure 34: The scheme of the SCLC characteristic of the insulator with traps distributed on one level. It shows (1) the ohmic region with thermal generation of carriers (~ $U^1$), (2) region of shallow mono-energy traps (~ $U^2$), (3) region of traps filling and (4) the region with filled traps (≈$U^2$). The dashed curve represents situation with the presence of very deep trap [53].*

#### *3.3.1.2 Physical Vapour Deposition (PVD)*

This method is used to deposit a thin film of material. Typically the thickness of the thus formed coating lies in the range of few nanometres to several micrometres. Based on the source material, the deposited films can include a range of chemical compositions. The deposition process consists of 3 steps. First, the applied material is evaporated from a solid source assisted by high temperature vacuum or gaseous plasma. Then, the vapours are transported in vacuum to the substrate surface and condensate here to generate thin film. These three fundamental steps are utilized by different PVD technologies, but the methods used to generate and deposit material may be different. The most common are thermal evaporation and sputtering. The first mentioned process is based on heating material using suitable methods in vacuum. The latter is a technique where the vapour is created from the source target by its bombarding with accelerated gaseous ions. One of the biggest advantages of PVD is this process is environmentally friendly [56].

### 3.3.2 Sample Preparation

#### *3.3.2.1 The Effect of Photoswitchable Charge Carrier Traps*

For observation of the influence of the photochromic molecule to the electrical properties of the polymeric matrix after its incorporation within it, diode like structures consisted of 5 components (glass slide and 4, respectively 5 thin layers) were prepared, see Figure 35. The effect of photochromic conversion and so of photoswitchable charge carrier traps to the mobility of charge carriers was monitored using the structures consisted of glass slide, transparent ITO electrode, PEDOT:PSS as a hole transport layer, pure or doped polymer as active layer and aluminium electrode. Its preparation involved several steps. At first, glass slides with transparent conductive ITO layer were cleaned by a series of ultrasonic baths, first one containing NaOH followed by the distilled water and the isopropyl alcohol. Such treated slides were covered by the PEDOT:PSS layer. The deposition was performed by the spin-coating method at 5 000 rpm. Thus prepared substrates were heated for at least 10 min on the hot plate set to the temperature 115 °C, so that the all humidity evaporated. After that, the active layer was applied under the nitrogen atmosphere in the glovebox by the same process, using the solutions prepared by the same manner as in the case of samples for optical characterization, see Table 2. Then, this layer was covered by the aluminium electrode using vapour deposition method and the whole process was completed by epoxide encapsulation.

*Table 2: The composition of individual solutions together with the thickness of prepared layers.*

| Polymer matrix | Polymer content (mg) | Spiropyran content (mg) | Solvent amount (µl) | Layer thickness (nm) |
|---|---|---|---|---|
| PVK | 10,0 | 0 | 500 | 170±10 |
| Tg PPV | 2,5 | 0 | 500 | 610±60 |
| PCBTDPP | 2,5 | 0 | 500 | 150±30 |
| PCDTBT | 2,5 | 0 | 500 | 270±40 |
| PVK | 10,0 | 3,00 | 500 | 230±50 |
| Tg PPV | 2,5 | 0,75 | 500 | 720±20 |
| PCBTDPP | 2,5 | 0,75 | 500 | 280±20 |
| PCDTBT | 2,5 | 0,75 | 500 | 170±20 |

#### *3.3.2.2 The Effect of Photochromic Isomers to the Photogeneration*

The effect of the open and closed form of SP1 molecule to the photogeneration within the polymeric matrices was monitored using the structures consisted of glass slide, transparent ITO electrode, PEDOT:PSS as a hole transport layer, pure or doped polymer as active layer, calcium as an electron transport layer and aluminium electrode. The calcium was used due to its low work function that facilitates the separation of electron-hole pairs which is the essential process of photogeneration. To prepare these structures, the identical procedure as in the previous case was employed. The only difference was in the deposition of the calcium layer by the vapour deposition method.

To observe the effect of the photochromic isomers to the photogeneration, other structures were prepared. These structures as well as the preparation process were the same as in the previous case, the only exception was the presence of molecule PCBM within the active layer, for the purpose to facilitate the separation of electron-hole pairs even much more. The ration PCBM : polymer was 1 : 1. These structures were prepared using only polymers Tg-PPV and PCDTBT as an active layer.

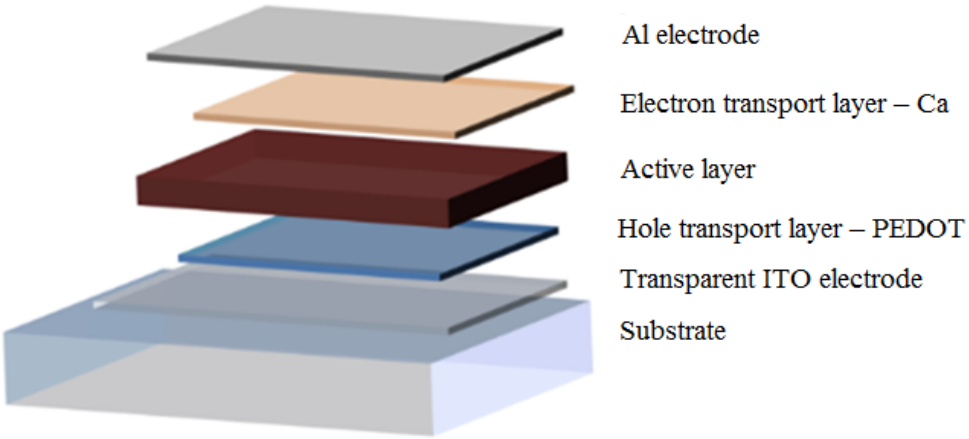



*Figure 35: The layers of the prepared diode like structures.*

### 3.3.3 Experimental Procedure

#### *3.3.3.1 The Effect of Photoswitchable Charge Carrier Traps*

To observe the effect of photochromic conversion and so of photoswitchable charge carrier traps to the mobility of charge carriers, the dark curves of prepared structures were obtained by the measurement by the electrometer Keithley 6517B. The applied voltage differed according to the material of polymeric matrix and according to the quality of active layer. After that, all of the samples were illuminated for 5 min by UV lamp with wavelength spectrum in the UVA spectral range. Hereby, the photochromic conversion was induced and the dark curves were obtained once again by the same measurement. This experiment was carried out with both, samples doped by photochromic SP1 and also with samples of pure polymers to observe which changes of I-V characteristics are caused by the degradation of polymeric matrix due to the UV light.

#### *3.3.3.2 The Effect of Photochromic Isomers to the Photogeneration*

The structures containing the layer of calcium together with the structure containing molecule PCBM were used to monitor the effect of the open and closed form of SP1 molecule to the photogeneration within the polymeric matrices. Again, the dark curves of these samples were obtained by the same measurement as in the previous case. After that, this measurement was repeated except it was conducted under solar simulator and so the illuminated curves were obtained. The light intensity was set 900 $W.m^{-2}$. Then, the photochromic conversion was UV-induced and dark curves together with illuminated ones were obtained once again. Both, structures whose active layer consisted of pure polymer as well as of doped material, underwent these measurements to observe which changes of I-V characteristics are caused by the degradation of polymeric matrix due to the UV light and not to improperly attribute them to the effect of spiropyran.

### 3.3.4 Results

#### *3.3.4.1 The Effect of Photoswitchable Charge Carrier Traps*

The aim of this part of electrical characterization was to observe the effect of photochromic conversion and so of charge carrier traps to the mobility of the charge carriers within various polymeric matrices. Therefore, the dark curves of the diode like structures whose active layer consisted of pure and SP1 doped polymers PVK, Tg PPV, PCBTDPP and PCDTBT before and after UV induced photochromic conversion were obtained, see Figure 36 – Figure 39. These I-V characteristics are shown in logarithmic as well as in linear scale.

The dark curves obtained for the structure whose active layer consisted of doped polymer PVK show significant decrease of current flowing through it after UV irradiation. This decrease is of one to one and half order of magnitude. In the area around 2 V, the current started to increase toward the initial curve, see Figure 36. The same phenomenon was observed for the structures containing polymer Tg PPV and PCDTBT, see Figure 37 and Figure 39. These curves show the decrease of one and two orders of magnitude after UV irradiation of the structure. The current started to increase in the region around 0,8 V and 2,8 V respectively. In the case of structure containing doped polymer PCBTDPP, the dark curves before and after UV irradiation are almost equal, see Figure 38. Even a little bit more pronounced difference was observed for the structure with pure polymer.

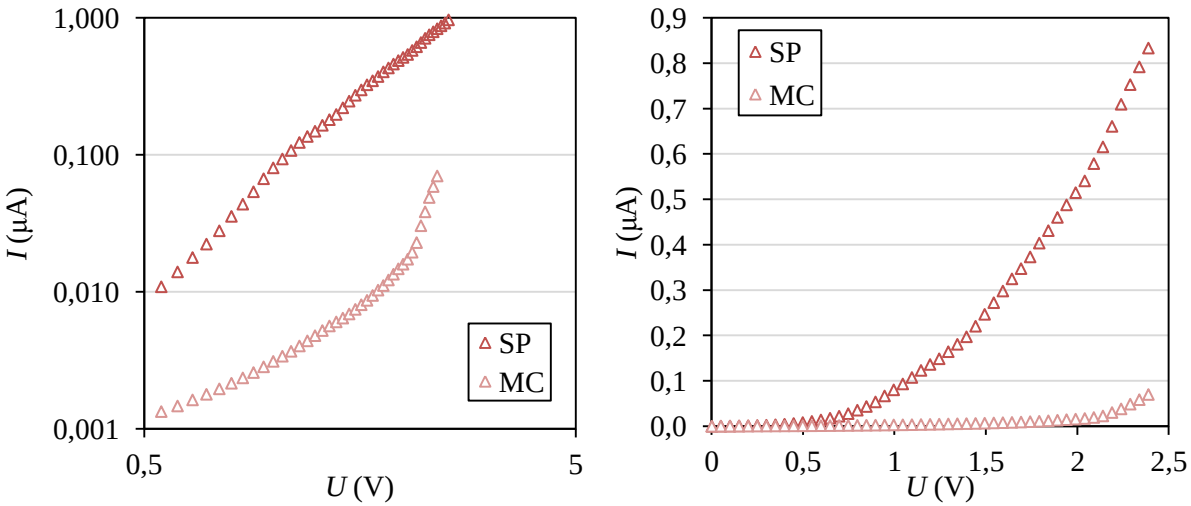



*Figure 36: The effect of photoswitchable charge carrier traps to the mobility of the charge carriers within the polymer PVK; dark curves with a logarithmic (left) and linear (right) scale.*

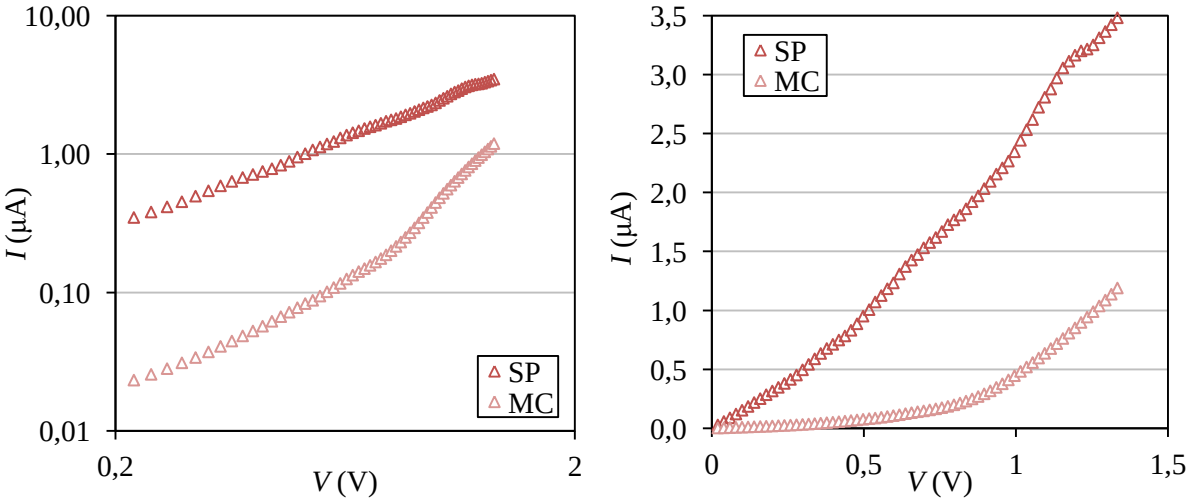



*Figure 37: The effect of photoswitchable charge carrier traps to the mobility of the charge carriers within the polymer Tg PPV; dark curves with a logarithmic (left) and linear (right) scale.*

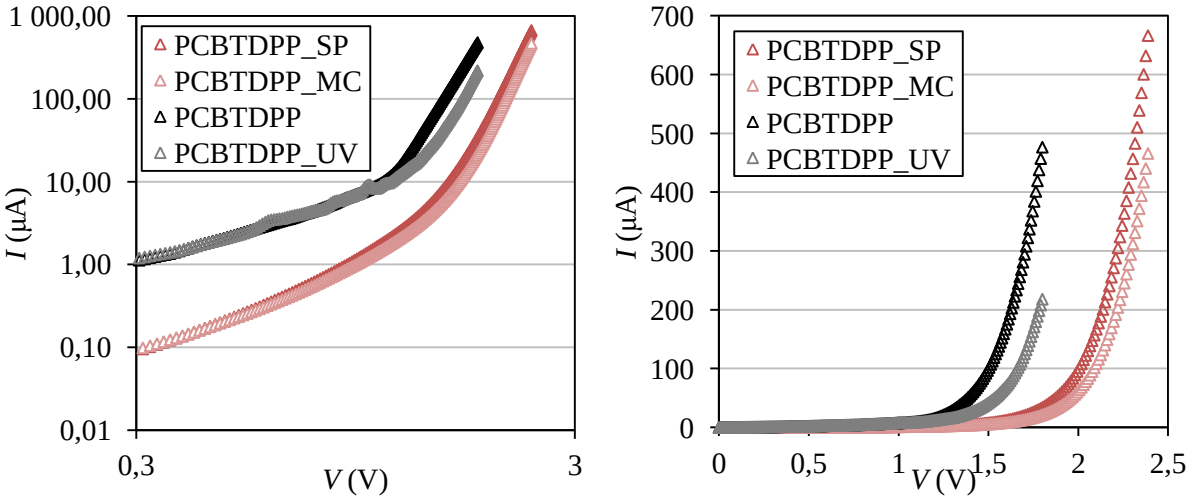



*Figure 38: The effect of photoswitchable charge carrier traps to the mobility of the charge carriers within the polymer PCBTDPP, together with I-V characteristics of structure containing pure polymer; dark curves with a logarithmic (left) and linear (right) scale.*

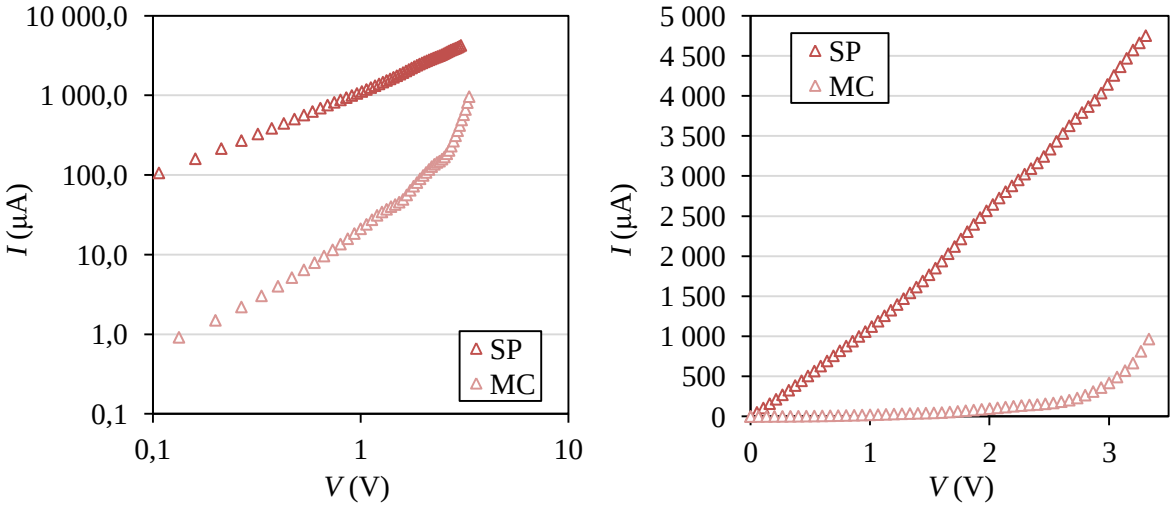



*Figure 39: The effect of photoswitchable charge carrier traps to the mobility of the charge carriers within the polymer PCDTBT; dark curves with a logarithmic (left) and linear (right) scale.*

*Discussion*

The considerable decrease of current flowing through the samples containing doped polymer PVK induced by UV light may be, according to the above mentioned theory, interpreted by the increased dipole moment of the photoproduct (MC) that acts as a trap for charge carriers within polymer chain, see Figure 36. The increase of the current in the area around 2 V suggests to the fill of these traps. Exactly the same influence of merocyanine form to the electrical properties of polymer matrix was proved after its incorporation into polymers Tg PPV and PCDTBT, see Figure 37 and Figure 39. The biggest difference between dark curves before and after UV irradiation was obtained for the cell whose active layer consisted of polymer PCDTBT. The photochromic conversion caused decrease of current flowing through this cell by two orders of magnitude. On the other hand, the I–V characteristics obtained in the dark for structure containing doped polymer PCBTDPP do not exhibit changed electrical properties caused by creation of merocyanine form, see Figure 38. Whereas, there is appreciable difference between curves obtained before and after UV irradiation of sample with pure polymer. This change was therefore considered to be caused by degradation of the material due to the UV radiation. The fact, that the effect of merocyanine was detected within three of four doped polymer matrices proved the above mentioned theory that the response of photochromic structure is affected by its environment.

### *3.3.4.2 The Effect of Photochromic Isomers to the Photogeneration*

The aim of this part of electrical characterization was to found out if the open and closed form of photochromic SP1 influenced the photogeneration within the polymeric matrix. Therefore, the dark and illuminated curves before and after UV-induced photochromic conversion were obtained for the structures whose active layer consisted of pure or SP1 doped polymers PVK, Tg PPV, PCBTDPP and PCDTBT, as well as for these structures contained moreover molecules PCBM, see Figure 40 – Figure *42*. These I-V characteristics are in linear scale. In the case of samples whose active layer was formed by the polymers PVK and Tg PPV, the illuminated curves were not affected by the photochromic conversion and so the photogeneration within these two matrices was not influenced as well. That is the reason, why their I-V characteristics were not included into the thesis.

The initial I–V curves of the structure containing doped polymer PCBTDPP as an active layer exhibit just a small increase of the current flowing through the sample under illumination compared to the dark curve. After the UV irradiation, the illuminated curve shows a slight increase

of the current, while dark curve was not affected by the UV irradiation at all, see Figure 40. In the area around 2 V, the illuminated curve obtained after exposure to the UV light started to copy the course of the initial curve. The changes of observed curves are much more significant in the case of sample containing polymer PCDTBT. After UV irradiation, the current flowing through the structure in the dark decreased, while under solar simulator illumination the current considerably increased.

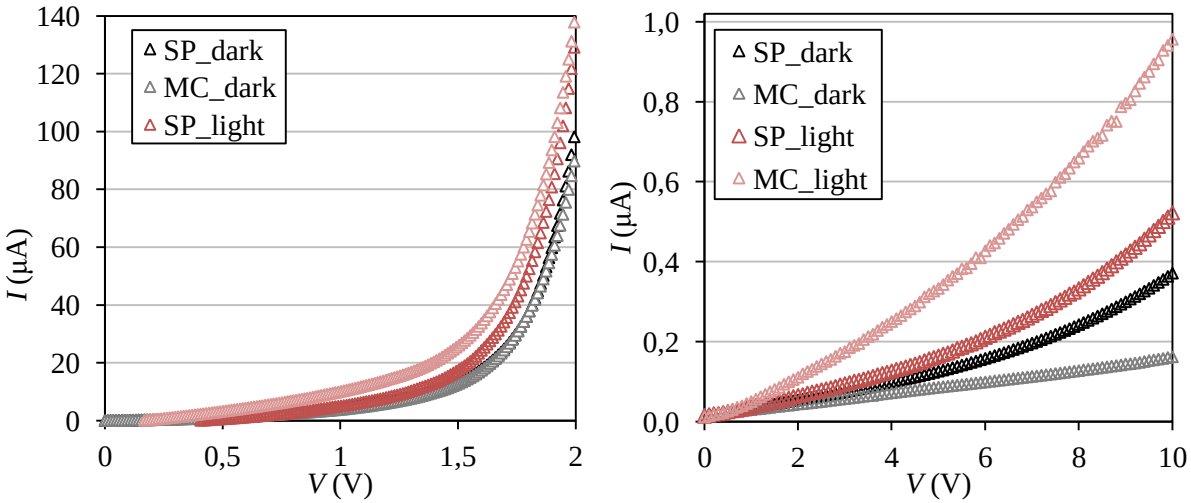



*Figure 40: The influence of photochromic isomers on photogeneration within polymer PCBTDPP (left) and PCDTBT (right); linear scale.*

The initial I-V curves obtained for the samples contained molecules PCBM show better photoconductivity compared to the previous ones, see Figure 41 and Figure 42. After the UV irradiation and so after inducing of merocyanine form creation, the current flowing through these samples increases in a certain area by approximately two orders of magnitude and its value is about the same in the dark as well as under illumination. The same phenomenon was observed for the sample containing both, polymer Tg PPV and polymer PCDTBT.

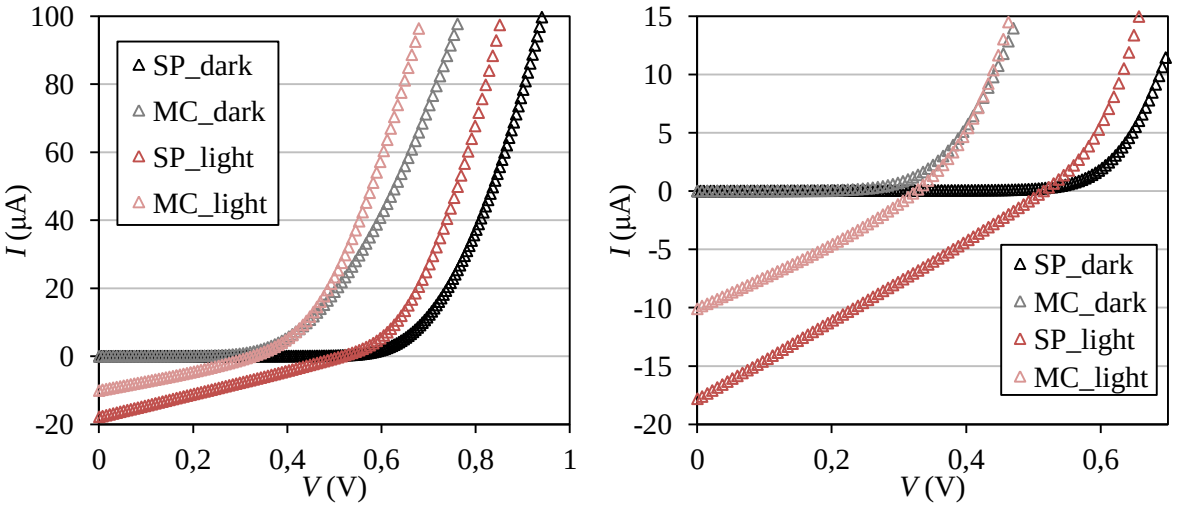



*Figure 41: The influence of photochromic isomers in combination with PCBM on photogeneration within polymer Tg PPV (left), together with the detail of selected area (right); linear scale.*

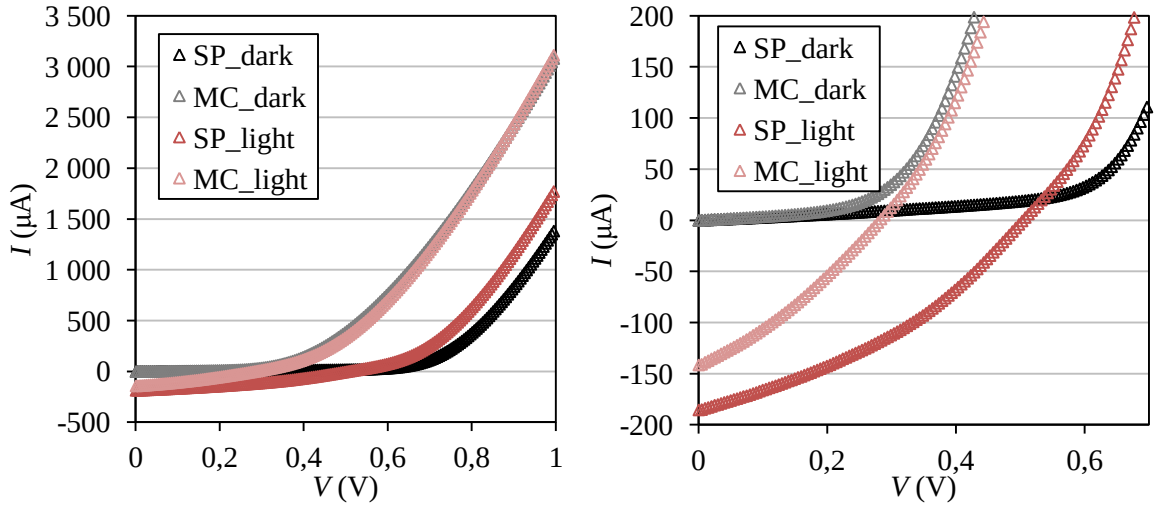



*Figure 42: The influence of photochromic isomers in combination with PCBM on photogeneration within polymer PCDTBT (left), together with the detail of selected area (right); linear scale.*

*Discussion*

The effect of the open and closed form of photochromic to the photogeneration within various matrices was observed. The sample containing doped polymer PCBTDPP as a polymeric matrix exhibit just a small increase of the current flowing through the sample due to the photogeneration, which indicates it is minimally photoconductive, see Figure 40. The illuminated curve reflecting changes that took place within the sample after photochromic conversion shows increase of flowing current. It denotes that merocyanine form has a positive effect to the photogeneration within polymer PCBTDPP. On the other hand, the dark curve obtained after UV irradiation proved the above mentioned statement, that samples consisting of doped polymer PCBTDPP do not exhibit changed electrical properties in the dark that will be caused by creation of merocyanine form, because this curve is almost identical to the one obtained before UV irradiation.

The same positive effect of merocyanine to the photogeneration was observed for the structure consisting of PCDTBT, see Figure 40. In this case, open photochromic isomer influenced the electrical properties of polymer matrix in the dark as well as under illumination. Obtained dark curves denote formation of trap for charge carriers within the polymer chain after UV irradiation due to the decreased flowing current. Again, the photoconductivity of this sample is minimal according to the curves measured before photochromic conversion. However, the flowing current significantly increases under illumination in the presence of photoproduct that indicates it positively affects the photogeneration. The possible explanation is that the structure of merocyanine acts as an acceptor of electrons generated under illumination within the polymer matrix.

The fact, that the photogeneration was influenced by the open and closed form of photochromic SP1 after its incorporation within different matrices just for two of these matrices again confirmed that the photochromic activity is strongly influenced by its environment.

The interesting results were obtained for the samples whose active layers consisted of polymer doped by SP1 together with PCBM, where after the UV irradiation and so after inducing of merocyanine form creation, the current flowing through these samples increases in a certain area by approximately two orders of magnitude and its value is about the same in the dark as well as under illumination, see Figure 41 and Figure 42. The possible explanation for this effect is the merocyanine form acts as an acceptor of generated electrons and transmits then to the structure of PCBM which leads to the improved photogeneration. To understand the exact mechanism of the process of this phenomenon, it will be necessary to conduct other experiments.

### 3.3.5 Summary of Electrical Characterization

The influence of the photochromic molecule to the electrical properties of the various polymeric matrices after its incorporation within them was studied. The effect of photochromic conversion and so of photoswitchable charge carrier traps to the mobility of charge carriers within polymers PVK, Tg PPV, PCBTDPP and PCDTBT was monitored. The obtained current-voltage characteristics of the structures containing doped polymers PVK, Tg PPV and PCDTBT as an active layer exhibit considerable decrease of current, flowing through them, induced by UV light. This phenomenon was attributed to the increased dipole moment that accompanied photochromic conversion and acts as a trap for charge carriers within polymer chain. In the particular area, the flowing current started to increase, which suggest the fill of formed traps. The current-voltage characteristics obtained for the structure containing doped polymer PCBTDPP as an active layer did not exhibit changed electrical properties caused by creation of merocyanine form.

The effect of the open and closed form of photochromic to the photogeneration within various matrices was observed. In the case of samples whose active layer was formed by the polymers PVK and Tg PPV, the photogeneration was not affected by the photochromic conversion. The structure containing doped polymer PCBTDPP exhibited minimal photoconductivity. The illumination by the UV light positively influenced the photogeneration within this matrix while obtained dark curve proved the statement that this polymer does not show changed electrical properties caused by the formation of charge carrier traps. The same positive effect of open form to the photogeneration was observed for the sample consisting of PCDTBT. The possible explanation is that the structure of merocyanine acts as an acceptor of electrons generated under illumination within the polymer matrix. According to the I-V curves obtained for this structure, the UV induced photochromic conversion affected its photogeneration as well as the mobility of charge carriers.

The positive influencing of the photogeneration was observed for the samples whose active layer consisted of the polymers Tg PPV and PCDTBT that are doped by the molecules SP1 and PCBM. These structures exhibit significant increase of the flowing current after UV irradiation, while its value is about the same in the dark as well as under illumination.

# 4 Conclusion

The main goal of this thesis was to incorporate the photochromic spiropyran SP1 into various polymeric matrices, namely into polymers PVK, Tg PPV, PCBTDPP and PCDTBT, and to observe if the presence of this structure leads to the change of its properties, attention was paid especially to the optical and electrical properties. Therefore, the thin layers of pure polymeric materials as well as layers of spiropyran-doped materials were prepared and their optical properties were studied by UV-VIS spectroscopy; the measurement of current-voltage characteristics provided information about electrical properties.

The photochromic activity of the molecule SP1 within varied polymeric matrices was studied. The ability of spiropyran to undergo UV induced photochromic conversion after its incorporation within individual polymers was monitored. The merocyanine form of photochromic was achieved after UV irradiation for all used matrices. According to the differential spectra, polymer PVK allows the highest yield of the photochromic conversion. This matrix is also the most suitable for observation of the concentration changes of merocyanine form within the sample by means of the absorption spectra, because it does not absorb wavelengths in its characteristic absorption area. On the other hand, this polymer absorbs in the characteristic absorption area of molecule SP1 and so it is difficult to observe the concentration changes of this structure. Conversely, the absorption spectra of other used polymers allows to monitor concentration changes of closed form and only with some restrictions, caused by the overlapping of absorption band of merocyanine with the band of polymers, the concentration changes of open form. The reverse conversion of merocyanine form to its initial structure induced by heat was studied as well. It was found that the initial photochromic structure was completely restored within matrices PVK and PCDTBT. The merocyanine form was little bit more stabilized while incorporated within polymer Tg PPV as a matrix, where together with the number of heating cycles the concentration of the initial form gradually increased, however, the initial concentration of the structure was not achieved. The greatest stabilization of open form was found while incorporated into polymer PCBTDPP, where the photochromic reverse conversion did not occur at all. This confirmed the theory, that the photochromic activity is very sensitive to their environment.

The influence of the photochromic molecule to the electrical properties of the various polymeric matrices after its incorporation within them was studied. The effect of photochromic conversion and so of photoswitchable charge carrier traps to the mobility of charge carriers within individual polymers was monitored. The obtained current-voltage characteristics of the structures containing doped polymers PVK, Tg PPV and PCDTBT as an active layer exhibit considerable decrease of current, flowing through them, induced by UV light, which was attributed to the UV-induced formation of traps for charge carriers within polymer chain. The current-voltage characteristics obtained for the structure containing doped polymer PCBTDPP as an active layer did not exhibit changed electrical properties caused by creation of merocyanine form. The effect of the open and closed form of photochromic to the photogeneration within various matrices was observed as well. The illumination by the UV light positively influenced the photogeneration within polymer PCBTDPP as a matrix. The possible explanation is that the structure of merocyanine acts as an acceptor of electrons generated under illumination within the polymer matrix. The same positive effect of open form to the photogeneration was observed for the sample consisting of PCDTBT. According to the I-V curves obtained for this structure, the UV induced photochromic conversion affected its photogeneration as well as the charge carrier mobility. The positive influencing of the photogeneration was observed also for the samples whose active layer consisted of the polymers Tg PPV and PCDTBT that are doped by the molecules SP1 and PCBM. These structures exhibit significant increase of the flowing current after UV irradiation, while its value is about the same in the dark as well as under illumination.

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